Development of New Nanofiltration Membranes

Thong Zhiwei

(B. Eng., National University of Singapore)

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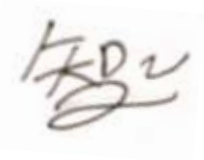
Supervisor:

Professor Chung Tai-Shung, Neal

Declaration

I hereby declare that this thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all the sources of information which have been used in the thesis.

This thesis has also not been submitted for any degree in any university previously.



Thong Zhiwei

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Summary

Faced with increasingly stringent regulations governing the discharge of wastewater containing heavy metal ions, various industries are demanding more efficient and effective treatment methods. Among the various existing methods, nanofiltration (NF) has been proven to be a feasible and promising option. However, the development of new NF membrane materials and applications is constantly required for the advancement of this technology.

To this end, in the first part of this dissertation, the development of a new composite NF membrane which comprises of a pentablock copolymer selective layer for the removal of heavy metal ions is explored. It has been observed that the incorporation of polyethyleneimine as the gutter layer between the selective layer and the substrate is necessary for the deposition of the selective layer onto the substrate. Subsequently, the deposition concentration of the pentablock copolymer is varied to optimise the performance. Due to the pentablock copolymer's unique ability to form a continuous water transport passageway with a defined pore size, the resultant NF membrane has a low molecular weight cutoff of 255Da with a reasonably high pure water permeability of 2.4LMH/bar. In addition, the newly developed membrane can effectively reject cations such as Pb^{2}+, Cd^{2+}, Zn^{2+} and Ni^{2+} (>98.0%) as well as anions such as $HAsO_4^{2-}$ (99.9%) and $HCrO_4^{-}$ (92.3%).

In the second part of this dissertation, the conceptual demonstration of the recovery of phosphates from sewage sludge to address the rapid depletion of mineral phosphorus has been carried out. The recovery of phosphates from

sewage sludge can be achieved by using a NF membrane which allows the preferential permeation of phosphate ions and the retention of toxic heavy metal ions. Hence, a NF membrane that is desirable for the phosphorus recovery have been fabricated by effectively controlled the interfacial polymerization between polyethyleneimine and TMC on a porous polyethersulfone ultrafiltration membrane substrate. A feed solution pH of lower than 2.1 is observed to be necessary for the required fractionation to occur. With an operating pressure of 10 bar and feed solution pH of 2, the newly developed NF membrane can reject heavy metal ions such as Cu, Zn, Pb and Ni (>93%) while still having a low phosphorus rejection of 19.6%. Assuming a permeate recovery of 90%, up to 90% of the feed phosphorus may be recovered using this newly developed NF membrane.

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List of Symbols and Abbreviations

A	Effective membrane filtration area
C_p	Permeate concentration
C_f	Feed concentration
DI	Deionized water
DBES	Doppler broadening energy spectroscopy
d_p	Mean effective pore diameter
d_s	Stokes diameters
FO	Forward osmosis
FESEM	Field emission scanning electron microscopy
IEC	Ion exchange capacity
MF	Microfiltration
MD	Membrane distillation
MWCO	Molecular weight cutoff
NMP	N-methyl-2-pyrrolidineone
NF	Nanofiltration
PES	Polyethersulfone
PEG	Polyethylene glycol
PIP	Piperazine
PEI	Polyethyleneimine
PAS	Position annihilation spectroscopy
PWP	Pure water permeability

pI	Isoelectric point
ΔP	Trans-membrane pressure
RO	Reverse osmosis
R	Effective rejection
TFC	Thin-film composite
TMC	Trimesoylchloride
UF	Ultrafiltration
σ_p	Geometric standard deviation

1 Chapter 1 Introduction

1.1 Overview of membrane technology

In the 21st century, environmental degradation, hunger and lack of drinking water represented some of the biggest problems for the world. The current situation is expected to be further aggravated in the near future by rapid population growth and economic development. These challenges prompted the various industries and governments to search for new technologies which enable the more efficient production of drinking water and food and the more effective protection of environment and human health. Among the various green technologies, membrane technology is one that has gained great importance over the past decades by replacing or complementing the conventional separation methods. This is mainly because membrane technology provides advantages such as reduced energy consumption [1, 2] and selective permeation.

In a typical membrane separation process, an effective driving force such as pressure difference, concentration and temperature is applied upon the feed mixture to enable the preferential permeation of one or more components across the membrane. The compounds that do not pass through the membrane are collectively known as the retentate while those that do pass though the membrane are collectively known as the permeate. It can be observed that the heart of any membrane separation processes is the membrane itself. The membranes enable the selective permeation of one or more components across it to achieve the required separation, and they can be categorized into various groups based on their materials, structures (types) and processes.

1.1.1 Membrane types

Membranes can be classified as isotropic or anisotropic depending on the homogeneity of their structure as seen in Figure 1.1a [3]. Isotropic membranes may be dense or highly porous. Dense isotropic membranes are often used in gas separation and rarely in water purification. This is because although they have high selectivity, they have relatively low flux due to their high transport resistance. In contrast, highly porous isotropic membranes are often used for rejecting particles which are larger than the membrane pore size via the size exclusion mechanism [3]. They are highly porous with pore size of less than 10μm in diameter. Although they may have high flux, they often suffer from low selectivity.

In order to achieve high selectivity and flux with reasonable mechanical stability, anisotropic membranes which usually consist of a thin selective layer and a thick porous support have been developed via various fabrication methods [3]. The thin selective layer and thick porous support can be developed via a single or multi-step operation. The fabrication of anisotropic membranes via a single step operation typically involves either temperature or non-solvent induced phase inversion methods. On the other hand, multi-step fabrication of anisotropic membranes often involves the separate preparation of the support and selective layer. This enables the independent control of the two layers. Such membranes are also known as composite membranes. In addition, membranes can be classified as hollow fiber or flat sheet membranes depending on their configuration Figure 1.1b [3].

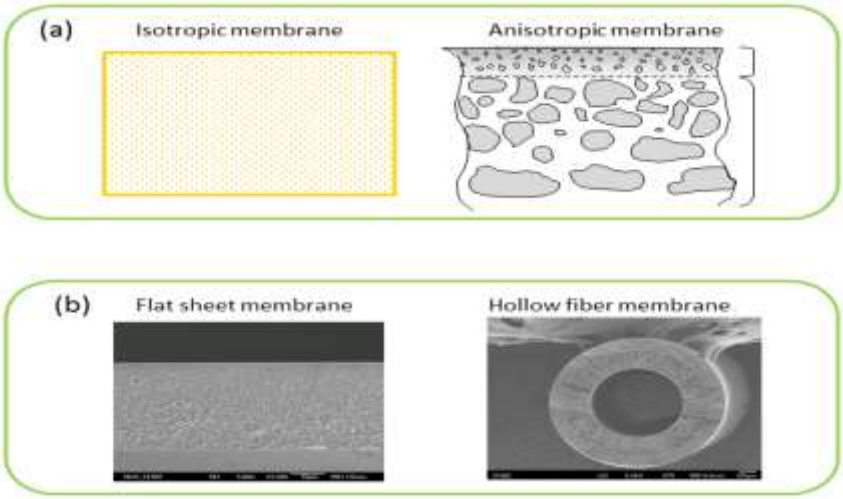

Figure 1.1 (a) Schematics of isotropic and anisotropic membranes and (b) electron microscopy image of flat sheet and hollow fiber membranes.[3]

1.1.2 Membrane processes

Traditional pressure-driven membrane processes for liquid based separation may be classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) depending on the pore size of the selective layer [3]. Table 1.1 summarizes their general characteristics such as pore size, operating pressure and separation mechanism. Among the various types of membranes, MF which has the largest pore size is utilized to remove large particles such as bacteria and suspended solids from the feed solution. UF can be used to remove macromolecules such as viruses and proteins. In contrast, NF membranes are often used in the removal of dyes [4, 5], pharmaceuticals [6, 7] and divalent ions [8] while RO membranes are employed in desalination.

Table 1.1 Characteristics of pressure-driven processes.

	MF	UF	NF	RO
Pore Size (nm)	50-5000	1-100	0.5-2	<0.5
Operating Pressure (bar)	<2	1-5	5-20	10-100
Separation Mechanism	Size exclusion	Size exclusion	Size exclusion and Donnan exclusion	Size exclusion and Solution diffusion

Membrane distillation (MD) and forward osmosis (FO) are 2 emerging membrane processes for liquid based separation. Unlike the use of hydraulic pressure as the driving force, MD is driven by the difference in water vapour pressure and temperature across the membrane. MD membranes have pore sizes similar to the MF membranes [3]. On the other hand, FO utilises the osmotic pressure difference between 2 different solutions to achieve desalination or wastewater reclamation [9-11]. The FO membranes may have either RO or NF pore size depending on the application [3].

1.2 Nanofiltration and its applications

It should be noted that particular attention shall be placed on NF membranes in this thesis due to its unique separation capabilities. Firstly, NF, which has a nominal molecular weight cutoff (MWCO, the molecular weight of solute that is 90% rejected by the membrane) ranging from 200 to 1000Da and pore size ranging from 0.5 to 2.0nm, is often considered as the intermediate process between UF and RO. Thus, it can offer higher rejection compared to either the UF or the MF but with lower pressure requirement compared to the RO [12, 13]. Secondly, unlike the other membrane types, the NF membranes' separation mechanism involves not only the size exclusion mechanism but also the Donnan exclusion mechanism (electrostatic repulsion) [14-16]. Hence, NF membranes can reject relatively small organic molecules and divalent ions while allowing monovalent ions to pass through.

As a result of its unique separation capabilities, the application range of NF has been growing rapidly since its introduction in the late 1980s. It is initially being employed in water softening and organics removal [3], but has

since then being widely used in numerous other applications such as pharmaceutical purification [6], removal of dyes from textile wastewater [4], heavy metals removal [1, 16-18], and treatment of organic solvent systems [3, 19].

However, this thesis shall focus on the applications of NF membranes in heavy metals removal. This is because heavy metals pollution has become a major problem in numerous countries due to the indiscriminate discharge of untreated wastewater. Wastewater containing heavy metals is produced by a great variety of modern industries such as the mining industry, batteries manufacturing and metal finishing. Lead (Pb), cadmium (Cd), mercury (Hg), copper (Cu), zinc (Zn), nickel (Ni) and chromium (Cr) are some common heavy metals found in the wastewater. The fact that heavy metals are highly toxic, non-biodegradable and tend to be bio-accumulated in living organisms serves only to further compound this problem. Although there is no general agreement between the various governments on the way to deal with it, there is a growing consensus among the world population that there is a need to prevent heavy metal pollution to prevent the environment and human health. In addition, the presence of heavy metals in wastewater hinders the reuse of wastewater and recovery of phosphorus from sewage sludge [20-23]. Consequently, increasing stringent regulations oblige industries to install effective wastewater treatment systems, and NF seems to be a promising option for the treatment of wastewater containing heavy metals.

1.3 Fabrication of NF membranes

Traditional NF membranes are typically anisotropic membranes and are fabricated mainly in 2 ways. One will consist of the one step phase inversion of cellulose acetate [3]. Another is a multistep operation during which a thin polyamide selective layer is formed via interfacial polymerization upon a highly porous substrate [3, 24]. The former NF membranes can be easily fabricated at low cost but suffer from comparatively lower flux and rejection. The latter, which is also known as thin film composite (TFC) membranes, generally possess higher flux and rejection than the former but are often negatively charged [16]. Thus, they may not be suitable for the removal of heavy metal ions which tends to be positively charged.

1.4 Research objectives and thesis organization

Recognising the potential of NF for the removal of heavy metal ions, this dissertation aims to (1) develop the suitable positively charged membranes for removal of heavy metal ions and (2) broaden the applications of the NF. There are a total of 4 chapters in the dissertation. Chapter One provides a general introduction to this study, which includes an overview of the membrane technology, introduction to NF and the necessity of this study. Chapter Two summarizes all the materials and methods that have been employed in this research project. The materials, membrane fabrication procedures and membrane characterizations methods shall be described in greater details. Chapter Three presents the possibility of using a molecularly designed Nexar^{TM} copolymer as the selective layer of a composite NF membrane. Various fabrication parameters have been optimised to enhance the membrane performance. Eventually, the possibility of using the newly

developed membrane for the removal of heavy metal ions is explored and promising results have been obtained. In Chapter Four, the application range of NF is broadened with the development of a NF membrane which is desirable for phosphorus recovery. During the recovery of phosphorus from sewage sludge, the NF membrane should be able to reject the various heavy metal ions while allowing the phosphorus to pass through. Purification of the phosphorus will then be achieved. The newly developed NF membrane is found to be able to effectively reject a wide variety of heavy metal ions such as Cu, Zn, Pb and Ni (>93%) while demonstrating a low phosphorus rejection of 19.6%. Promising results have been obtained.

2 Chapter 2 Materials and Methods

2.1 Materials

The commercially available polymer Matrimid® 5218 (Vantico Inc.) and polyethersuflone (PES) polymer (Solvay Advanced Polymer, LLC) were utilized to fabricate the membrane substrate. Both the pore former polyethylene glycol 400 (PEG 400, MW = 400 $gmol^{-1}$) and solvent N-methyl-2-pyrrolidineone (NMP, >99.5%) were purchased from Merck. They were used as received for the dope preparation. Hyperbranched polyethyleneimine (PEI) with molecular weights of 800 $gmol^{-1}$ (PEI 800, Sigma-Aldrich), 2000 $gmol^{-1}$ (PEI 2K, Sigma-Aldrich), 25000 $gmol^{-1}$ (PEI 25K, Sigma-Aldrich) and 60000 $gmol^{-1}$ (PEI 60K, Acros) and trimesoylchloride (TMC, >98% Sigma-Aldrich) were used as the monomers for the interfacial polymerization reaction in Chapter Four. However, PEI 60K was also used as the cross-linking agent of Matrimid® in Chapter 3. The sulfonated pentablock copolymer solution (11 wt% in a mixed solvent of heptane and cyclohexane) with an ion exchange capacity (IEC) of 1.5 was prepared and provided by Kraton Polymers LLC (USA). N-hexane ordered from Avantor was either used as the solvent for TMC to form the organic solutions or employed to dilute the sulfonated pentablock copolymer solution to the required concentration. Ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polyethylene oxide, glucose and sucrose, supplied by Sigma-Aldrich, were employed to determine the pore size distribution of the membrane. NaCl (Merck), $MgCl_2.6H_2O$ (98%, Alfa Aesar), $Pb(NO_3)_2$ (99%, Acros), $CdCl_2$ (Acros), $NiCl_2$ (98%, Acros), $CuSO_4$ (Sigma-Aldrich), $ZnCl_2$ (98%, Sigma-Aldrich), $Na_2Cr_2O_7$ (Merck), Na_2HAsO_4 (98%, Sigma-Aldrich)

and H_3PO_4 (85%, Merck) were utilized to characterize the transport properties of various salts across the membranes. Nitric acid (HNO_3, >69.0% Sigma-Aldrich) and sodium hydroxide (NaOH, >97% Sigma-Aldrich) were used to adjust the pH of salt solutions. On the other hand, hydrochloric acid (HCl, 37% Sigma-Aldrich) and sodium hydroxide (NaOH, >97% Sigma-Aldrich) were prepared in aqueous solutions for the zeta-potential measurements. Deionized water (DI) used in this study was produced by a Milli-Q ultrapure water system (Millipore, USA).

2.2 Fabrication of substrate

The PES and Matrimid® flat-sheet membrane substrates were both fabricated via a non-solvent induced phase inversion method [10, 25]. This would involve the casting of a polymer dope, which contains polymer/pore former/non-solvent/solvent at certain ratio, onto a clean glass plate with a 100µm tall casting knife. The entire assembly was then immersed in a water bath for phase inversion to occur. After which, the newly fabricated membrane was soaked and preserved in DI water to remove the residual NMP and PEG 400.

2.3 Membrane characterizations

2.3.1 Membrane morphology

The field emission scanning electron microscopy (FESEM, JEOL JSM 6700) was utilized to examine the cross-section and surface morphology of the membrane. During the sample preparation, the membrane was first dried with a freeze-dryer before being fractured in liquid nitrogen. The fractured samples were then subjected to platinum sputtering using a JEOL JFC-1100E ion sputtering device before being mounted onto the FESEM for examination.

2.3.2 Membrane microstructure

The membrane micro-structure as a function of depth was investigated using the Doppler broadening energy spectroscopy (DBES) that was generated using a Position annihilation spectroscopy (PAS) coupled with a variable mono-energy slow positron beam. For each membrane sample, the DBES would have consisted of 29 distinct spectra which were obtained at different positron incident energy (0-30eV). An HP Ge detector (EG & G Ortec) was employed to detect the spectra with a counting rate of about 1000 counts per second, and a total of 1.0 million counts were recorded for each individual spectrum.

In this study, the depth profiles of the membranes were characterized by the *S* parameter of the DBES, which refers to the ratio of the integrated counts between 510.3 and 511.7keV. Given that the *S* parameter is related to the relative value of the low momentum section of the positron-electron annihilation radiation, it reflects the changes in the chemistry and free volume of the membranes. Hence, both the chemistry and free volume change of the membrane, as a function of depth, can be determined using the *S* parameter. More information regarding the use of PAS can be found in other publications [26, 27].

2.3.3 Membrane surface charge

The surface charge of membranes as a function of pH was calculated based on the streaming electric potential measurements using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria). This was achieved by pumping a 0.01M NaCl electrolyte solution through the measuring cell containing the membrane with the pH of the electrolyte solution constantly

being adjusted via auto titrations with 0.1M NaOH and 0.1M HCl. Subsequently, the isoelectric point (p*I*) of the membrane was determined based on the relationship between the pH and surface charge.

2.3.4 Pure water permeability (PWP), salt rejection tests, pore size and molecular weight cutoff (MWCO)

The pure water permeability (PWP, LMH/bar) of membranes was evaluated using dead-end stainless steel filtration cells at room temperature with an effective membrane area of 3.14cm^2. A transmembrane pressure, ΔP, of 10.0bar at room temperature was usually applied during the test unless otherwise stated, and the PWP of membranes was calculated using Equation 1:

$$PWP = \frac{V}{At\Delta P} \quad (1)$$

where V (L) is the permeate volume collected within a time period, t (h), while A (m^2) is the effective membrane filtration area and ΔP (bar) is the applied trans-membrane pressure. All the membranes were stabilized for at least 1 hour before measurements. Furthermore, to ensure the reproducibility, more than 3 individual membrane samples were prepared for each experimental condition, and the average results were reported in this study.

On the other hand, the salt rejections of membranes were determined using model solutions of NaCl, $MgCl_2$, $Pb(NO_3)_2$, $CdCl_2$, $NiCl_2$, $CuSO_4$, $ZnCl_2$, $Na_2Cr_2O_7$, Na_2HAsO_4 and H_3PO_4 as feed solutions individually. The model solutions only contain one target component at each time. Mixed solutions are not used in this study. The concentrations of the metal and phosphorus elements were kept at 1000ppm for easy comparison of performance with other membranes. HNO_3 and NaOH buffer solutions were prepared and used to adjust the pH of the salt solutions when necessary. A

transmembrane pressure, ΔP, of 10.0bar at room temperature was usually applied during the test unless otherwise stated. All the membranes were stabilized for at least 1 hour before measurements. The concentrations of both the feed and permeate were evaluated using the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Optima 7300DV, PerkinElmer, USA), and the effective rejection R (%) for each salt was calculated using Equation 2.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where C_p and C_f are the solute concentrations of the permeate and feed, of PWP values, three or more samples were prepared for each experimental respectively. The solute may refer to anions, cations or organic solutes depending on the solute of interest. Similar to the determination condition and the average value was reported.

In contrast, the mean effective pore diameter (d_p) and molecular weight cutoff (MWCO) of each individual membrane were evaluated using the solute rejection experiments [28-30]. Various feed solutions consisting of 200 ppm organic solutes were used in this study. Depending on the pore size distributions of the membranes, different organic solutes could be used. Both PEG and PEO, which have larger Stokes diameters, were employed in determining the pore size distributions of the membrane substrates. In contrast, smaller organic solutes were used for the composite NF membranes. Table 2.1 summarizes the molecular weights (MW) and Stokes diameters (d_s) of the smaller organic solutes [16, 31]. The Stokes diameters of the PEG and PEO solutes were calculated by the following equations, respectively:

For PEG, $d_s = 33.46 \times 10^{-12} \times M^{0.557}, (MW \leq 35{,}000)$ (3)

For PEO, $d_s = 20.88 \times 10^{-12} \times M^{0.587}, (MW \geq 100{,}000)$ (4)

During testing, a transmembrane pressure of 10bar was also used to induce the permeation flow across the membrane. Pre-stabilization was taken before any measurement to minimize any dilution effect. A total organic carbon analyzer (TOC ASI-5000A, Shimazu, Japan) was used to determine the solute concentrations in both the feed and permeate. The effective rejection coefficient *R* (%) for each organic solute was obtained using Equation 2. Subsequently, the solute rejection *R* was plotted against the Stokes diameter on a log-normal probability paper to yield a straight line. Membrane molecular weight cut-off (MWCO), mean effective pore diameter (d_p) and the geometric standard deviation (σ_p) were determined from the straight line. The MWCO is defined as the molecular weight of the solute at which the rejection is 90% while μ_p is the pore diameters at which *R*=50% and σ_p is the ratio of the pore diameters when *R*=84.13% and 50%. After which, the pore size distribution of the membrane was evaluated using Equation 5:

$$\frac{dR(d_p)}{dd_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp\left[-\frac{(\ln d_p - \ln \mu_p)^2}{2(\ln \sigma_p)^2} \right] \quad (5)$$

where d_p is the pore diameter.

Table 2.1 Molecular weights and Stokes diameters of organic solutes used for the determination of the pore size distribution **[16, 31]**

Solute	**MW ($gmol^{-1}$)**	**d_s (nm)**
Ethylene glycol	62	0.470
Diethylene glycol	106	0.582
Triethylene glycol	150	0.668
Glucose	180	0.730
Surcrose	342	0.942

3 Chapter 3 Novel nanofiltration membranes consisting of a sulfonated pentablock copolymer rejection layer for heavy metal removal

This chapter has been published as a journal paper

Z. Thong, G. Han, Y. Cui, J. Gao, T. S. Chung, S. Y. Chan, S. Wei, Novel nanofiltration membranes consisting of a sulfonated pentablock copolymer rejection layer for heavy metal removal, Environmental Science & Technology 48, 13880−13887 (2014).

3.1 Summary

Facing stringent regulations on wastewater discharge containing heavy metal ions, various industries are demanding more efficient and effective treatment methods. Among the methods available, nanofiltration (NF) is a feasible and promising option. However, the development of new membrane materials is constantly required for the advancement of this technology. This is a report on the first attempt to develop a composite NF membrane comprising a molecularly designed pentablock copolymer selective layer for the removal of heavy metal ions. The resultant NF membrane has a mean effective pore diameter of 0.50 nm, a molecular weight cut-off of 255 Da and a reasonably high pure water permeability of 2.4 LMH/bar. The newly developed NF membrane can effectively remove heavy metal cations such as Pb^{2}+, Cd^{2+}, Zn^{2+} and Ni^{2+} with a rejection greater than 98.0%. On the other hand, the membrane also shows reasonably high rejections towards anions such as $HAsO_4^{2-}$ (99.9%) and $HCrO_4^{-}$ (92.3%). This performance can be attributed to (1) the pentablock copolymer's unique ability to form a continuous water transport passageway with a defined pore size and (2) the incorporation of polyethyleneimine (PEI) as a gutter layer between the selective layer and the substrate. To the best of our knowledge, this is the first reported NF membrane comprising this pentablock copolymer as the selective material. The promising preliminary results achieved in the current study provide a useful platform for the development of new NF membranes for heavy metal removal.

3.2 Introduction

As mentioned above, heavy metal pollution has become a major problem in numerous countries due to the indiscriminate discharge of

untreated wastewater. As such, there is an urgent need to address the current situation to prevent further damage to the environment and human health. Thus, in order to achieve effective removal of heavy metals and recycling of wastewater, various treatment technologies such as ion-exchange, chemical precipitation, adsorption, coagulation-flocculation, flotation, electrochemical methods and membrane filtration have been adopted [12, 17, 18, 32]. In particular, a lot of research has been conducted into membrane filtration technology [12, 18, 32] because it can provide (1) high removal efficiency, (2) easy operation and fabrication, (3) space saving, and (4) no phase change.

Among the membrane processes used, reverse osmosis (RO) and nanofiltration (NF) are common means of heavy metal removal [33]. Although RO rejects a wide variety of dissolved species, it suffers from the drawbacks of high operating pressure, high energy consumption and severe membrane fouling [14, 18, 32]. In contrast, NF processes are usually able to alleviate these issues by operating at a lower pressure while maintaining a high permeation flux and reasonable rejection. Various dissolved species can be effectively rejected by NF membranes via the size and the Donnan exclusion (electrostatic repulsion) mechanisms [7, 13, 15, 34]. Hence, NF has garnered renewed interest and may be a suitable treatment of heavy metal wastewater [35].

Currently, most NF membranes are thin-film composites (TFC) with an ultrathin polymeric film deposited onto the surface of an asymmetric porous substrate [24]. The porous substrate of the TFC membrane provides the necessary mechanical strength for the membrane to withstand the high operating pressure, while the ultrathin polymeric film achieves the rejection of

various dissolved species. Therefore, this asymmetric configuration enables the use of complementary materials and methods to modify each layer separately and optimize overall membrane performance [36]. However, it should be noted that the selective layer of the current state-of-the-art NF membranes predominantly consist of cross-linked networks of aromatic polyamide prepared by interfacial polymerization [37]. As few materials are suitable to form the rejection layer of composite membranes, we endeavor to develop novel membrane materials to produce more efficient and stable NF membrane for various applications.

The molecularly designed Nexar™ copolymer consisting of pentablock copolymer poly(*t*-butylstyrene-*b*-hydrogenated isoprene-*b*-sulfonated styrene-b-hydrogenated isoprene-*b*-*t*-butylstyrene) (tBS-HI-SS-HI-tBS) has several advantageous characteristics due to its unique structure. First, it can achieve a high degree of sulfonation without a significant loss of mechanical stability [38-42]. Second, the degree of sulfonation of the copolymer can be easily tailored for various applications. Third, the merging of the middle sulfonated styrene block to form a continuous water transport passageway during the film formation serves to further enhance the water permeability of the membrane [40-42]. Consequently, the purpose of this study is to develop an effective composite NF membrane which consists of the sulfonated pentablock copolymer as the thin selective layer and a polyethyleneimine (PEI) modified Matrimid® as the substrate. By effectively controlling the membrane preparation process, the composite membranes were designed to possess high water permeability and ion rejections. In addition, the heavy metal removal performance of these new NF membranes was evaluated using a variety of

heavy metal solutions and encouraging results are obtained. The positive results of this study may provide a useful platform for the fabrication of new NF membranes.

3.3 Materials and methods

3.3.1 Fabrication of Matrimid® substrate

The Matrimid® flat-sheet membrane substrates were fabricated via a non-solvent induced phase inversion method as described in Section 2.2. In summary, the Matrimid® polymer was first dried in a vacuum oven at 80 ^{o}C for 24 hours to remove all moisture. Next, the dried polymer (18 wt%) was dissolved in a mixture, which consists of the pore former PEG 400 (16 wt%) and solvent NMP (66 wt%), at 70^{o}C under stirring. The formed homogeneous polymer solution was degassed overnight before usage. Finally, the flat-sheet substrate membrane was fabricated via a lab-scale casting process. The as-fabricated membranes were then soaked in deionized water to remove the residual NMP and PEG 400.

3.3.2 Fabrication of composite NF membrane

During the fabrication of the composite NF membrane, the Matrimid® membrane substrate was first cross-linked by a PEI aqueous solution (3.0 wt%) at 70 ^{o}C for 1 hour. Next, the modified substrate was rinsed with deionized water to remove the unreacted PEI. For better illustration of the cross-linking reaction, the chemical structures of Matrimid® 5218, PEI and a possible product of the reaction are shown in Figure 3.1.

The copolymer selective layer was then formed on the modified substrate by depositing a copolymer solution with a required concentration onto the top layer for 1 min at room temperature (23 ^{o}C). Prior to the

deposition of the selective layer, the excess water on the surface of the membrane substrate was removed by a filter paper. The copolymer concentrations used in this study were 0.5, 1, 2, 3, 4 and 5 wt%. The resultant NF membranes were then allowed to stabilize in air for 5 min at room temperature (23 ^{o}C) before being immersed in ethanol for 1 hour to facilitate the removal of n-hexane. Finally, the membrane was soaked in deionized water to remove ethanol.

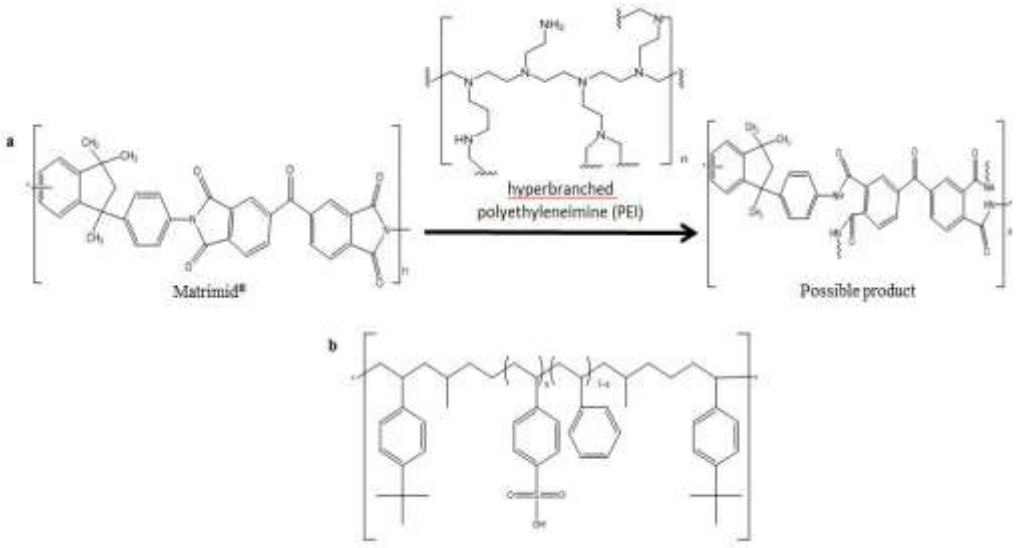

Figure 3.1 (a) Possible cross-linking reaction between Matrimid® and hyperbranched polyethyleneimine (PEI) and (b) chemical structure of pentablock copolymer.

3.4 Results and discussion

3.4.1 Fabrication of the effective membrane substrate

The morphology of the Matrimid® membrane substrate is shown in Figure 3.2. It can be observed that the substrate consists of a relatively dense top skin layer of ~250 nm in thickness and a highly porous and macrovoid-free cross-section. The top surface is relatively smooth with tiny pores of ~20 nm in diameter. The observed substrate morphology may have several advantages. Firstly, the sponge-like cross-section, together with the surface pores, may help to reduce the transport resistance and thus, achieving high

water permeation. In addition, the macrovoid-free cross-section also provides the substrate with robust mechanical properties to sustain the high pressure operations of NF.

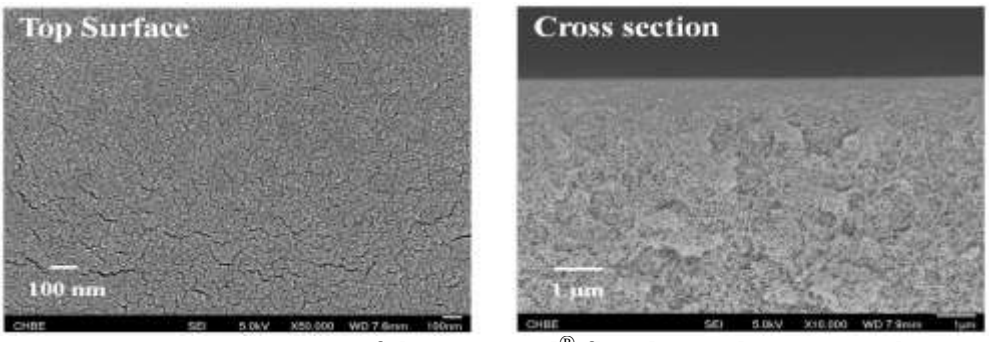

Figure 3.2 FESEM images of the Matrimid® flat-sheet substrate membrane.

However, the deposition of the pentablock copolymer directly onto the Matrimid® substrate is not advisable due to a number of reasons. It can be observed from Figure 3.3 that the zeta potential of the Matrimid® substrate decreases as the pH increases. The isoelectric point of the substrate is around pH 3.9, and the substrate is increasingly negatively charged above this point. Given that the pentablock copolymer copolymer may form a negatively charged dense film between pH 3 and 10 [42], the adhesion between the substrate and the selective layer may be less than ideal due to electrostatic repulsion. The long term stability of the membrane is questionable. In addition, as seen in Table 3.1, although the Matrimid® substrate has a high PWP of 478 LMH/bar, it has a relatively large mean effective pore diameter of 17.3 nm. This may not be ideal for the deposition of the active layer as severe solution intrusion may occur.

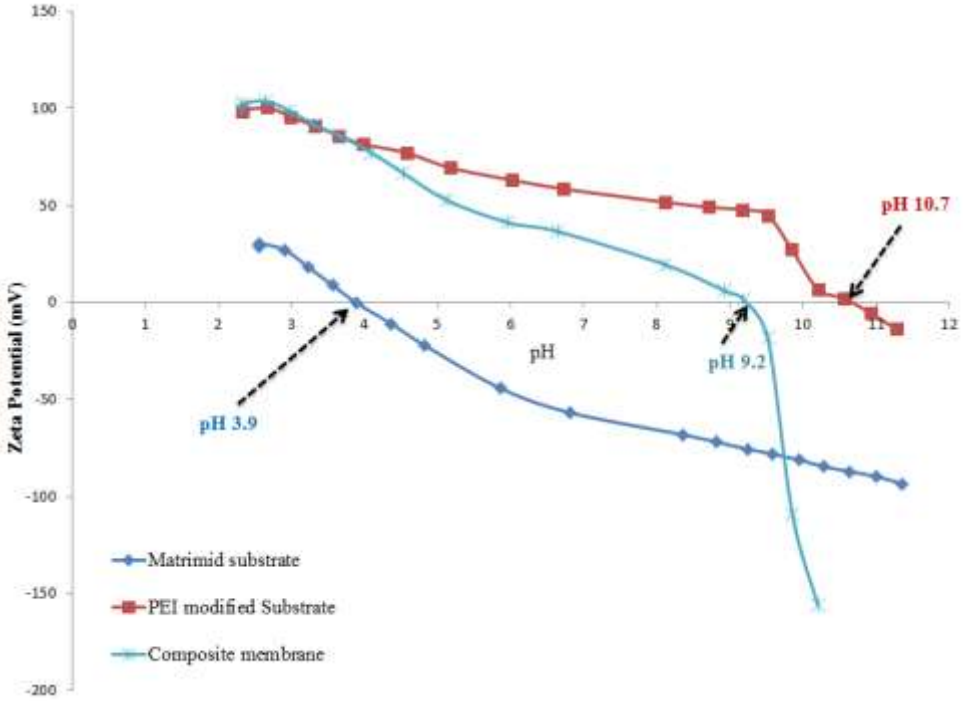

Figure 3.3 Zeta-potential vs. pH curves of the membranes. (Experiments were carried out with 0.01M NaCl. The composite membrane was obtained using a 3wt% deposition concentration and 1 min deposition time.)

Table 3.1 Mean Effective Pore Diameter (d_p), Geometric Standard Deviation (σ_p), Molecular Cut Off Weight (MWCO), Pure Water Permeability (PWP) and salt rejections of the membranes.

Membrane	μ_p (nm)	σ_p	MWCO (Da)	PWP (LMH/bar)	NaCl rejection (%)	$MgCl_2$ rejection (%)
Matrimid Substrate	17.3	1.23	148006	478 ± 52	≈0	≈0
Modified Substrate	14.9	1.39	133816	25.6 ± 4.2	11.9 ± 1.1	19.7 ± 8.9
Composite membrane*	0.50	1.45	255	2.4 ± 0.3	71.2 ± 3.9	96.5 ± 1.5

* The composite membrane was obtained using a 3wt% deposition concentration and 1 min deposition time.

Consequently, the thermal cross-linking of the Matrimid® substrate with PEI is introduced. As illustrated in Figure 3.1, during the cross-linking reaction, the highly branched PEI monomers are grafted onto the Matrimid® substrate via the formation of amide functional groups. The protonation of

these amine groups confers an overall positive charge to the substrate surface for a wide range of pH [6, 10, 43-45] Hence, it can be observed from Figure 3.3 that the modified substrate has an isoelectric point of around pH 10.7 and is highly positively charged for pH below 10.7. This may promote electrostatic attraction between the selective layer and the substrate and enhance the adhesion between them [45].

Besides, the PEI cross-linking may also serve to minimize the intrusion of the selective materials into the porous substrate. This is because the PEI cross-linking can effectively reduce the pore size of the substrate [6, 16]. As confirmed in Table 3.1, the mean effective pore diameter of the substrate decreases from 17.3 to 14.9 nm after the PEI cross-linking. This can also be observed from Figure 3.4 which depicts the probability density function curves of the different membranes with the peaks and the widths of the curves representing the mean effective pore diameters and the distributions of the pore diameters respectively. As seen in Figure 3.4 top, the peak shifted to the left after the PEI cross-linking, indicating a reduction of the mean pore diameter. As a result, the solution intrusion may be reduced during the deposition of the selective layer.

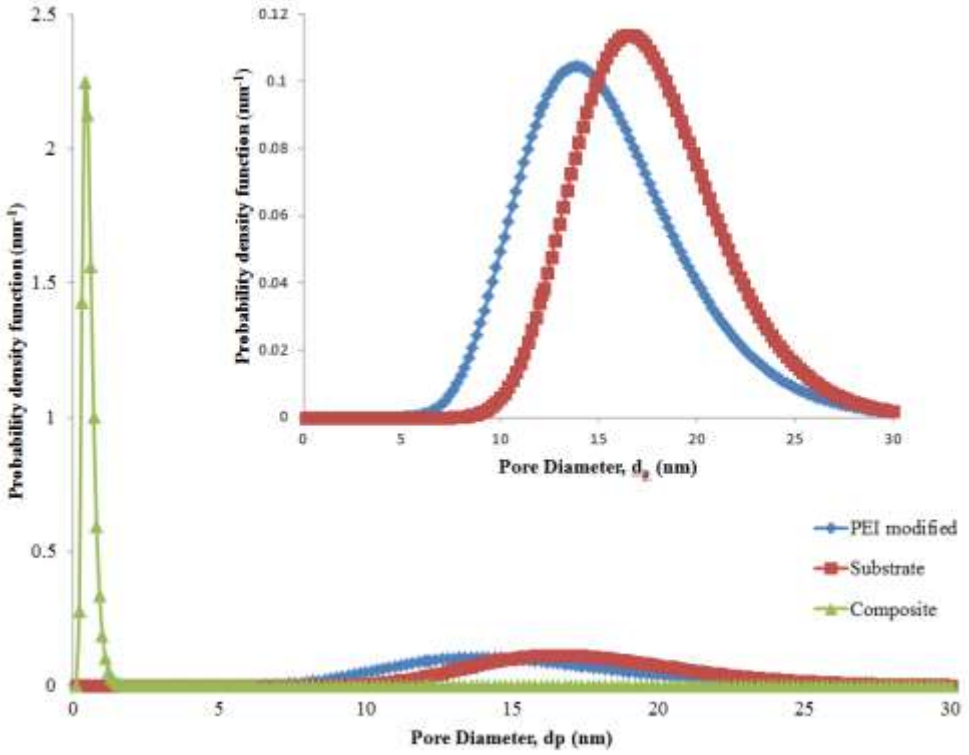

Figure 3.4 Probability density function curves of the membranes. (The composite membrane was obtained using a 3 wt% deposition concentration and 1 min deposition time.)

3.4.2 Fabrication of the composite NF membrane

Subsequently, a thin layer of the pentablock copolymer was deposited onto the PEI modified substrate to form the NF membrane. It was found that the copolymer could easily attach onto the membrane substrate within a short period of time. A thin selective layer with a very narrow pore size distribution is formed as shown in Figure 3.4 (bottom). There is a big shift of the pore size distribution to the left after the deposition of the selective layer. Hence, the PEI cross-linking plays a critical role. Without it, experimental data (not shown here) imply that it is hard to deposit a defect-free selective material on the substrate.

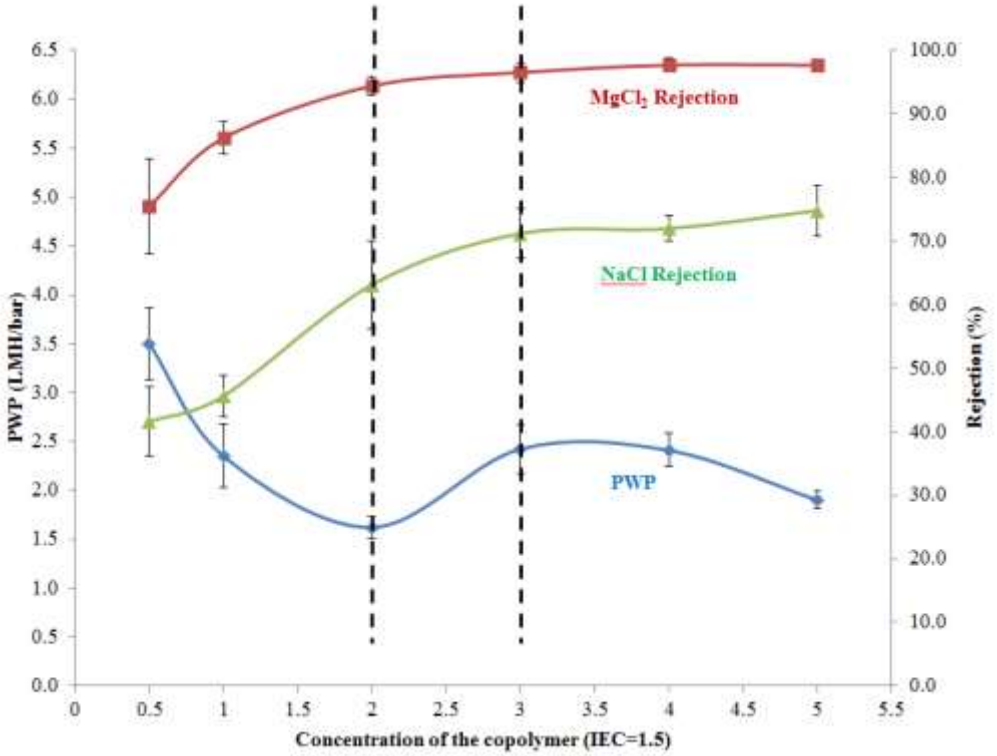

Figure 3.5 Effect of deposition solution concentration on the performance of the composite membranes

The effect of deposition solution concentration on membrane performance is illustrated in Figure 3.5. This was achieved by first depositing Nexar^{TM} copolymer solutions of various concentrations ranging from 0.5 to 5 wt% onto the PEI modified substrate with a fixed deposition time of 1min and then, examining the NF performance of the resultant membranes. 3 different zones are observed in Figure 3.5; namely, from 0.5 to 2 wt%, 2 to 3 wt% and 3 to 5 wt%. First, the PWP of the formed composite NF membranes decreases from 3.5 to 1.6 LMH/bar as the deposition solution concentration increases from 0.5 to 2 wt%. On the other hand, both the NaCl and $MgCl_2$ rejections increase from 41.6 to 63.2% and from 75.5 to 94.4%, respectively. This is possibly due to the increase in selective layer thickness which increases the transport resistance for both water and salts. The thickness of the selective layer is determined using their FESEM images. As illustrated in Figure 3.6,

the selective layer becomes much thicker as the deposition concentration increases. In addition, it can be clearly observed that a relatively continuous copolymer film consisting of nodules is obtained with a deposition concentration of 2 wt%. However, pinhole pores can still be observed on this surface and thus, slightly lower salt rejections are observed.

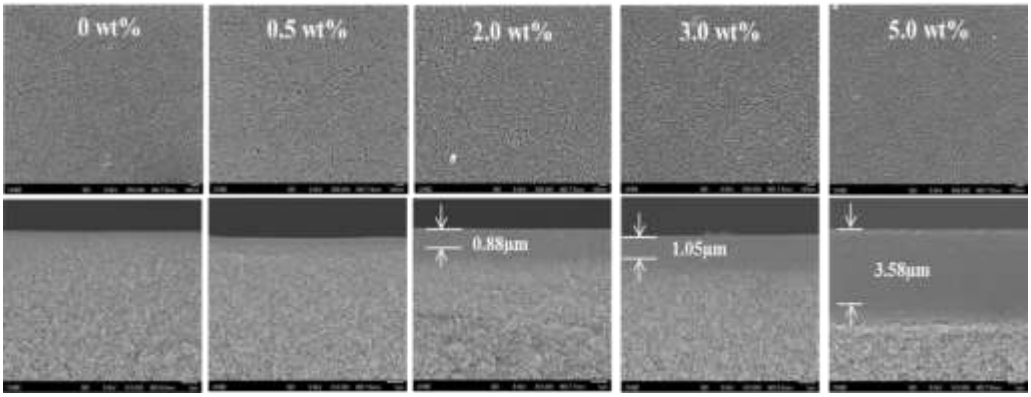

Figure 3.6 Surface and cross-section morphologies of the composite membranes as a function of polymer concentration.

When the deposition concentration is further increased from 2 to 3 wt%, the rejection of the composite membrane to NaCl also increases from 63.1% to 71.2%. A slight increase in the $MgCl_2$ rejection, from 94.4% to 96.5%, is also observed. However, it is interesting to note that the PWP increases from 1.6 to 2.4 LMH/bar despite an increase in the thickness of the selective layer. This is likely a result of the pentablock copolymer forming spherical micelles which consist of a sulfonated styrene core and a t-butyl styrene-b-hydrogenated isoprene corona in the nonpolar solvent system [40, 46-48]. During the deposition process, the copolymer spherical micelles will first adhere onto the substrate surface and then compact together when the solvent is evaporated. As a result of this compaction, some of sulfonated styrene cores may merged together to form interconnected sulfonated styrene micro-domains which can serve as water transport passageways [41]. This

structure reduces the water transport resistance of the selective layer and enables the composite membrane to achieve a significantly higher PWP of 2.4 LMH/bar without compromising the salt rejections.

However, when the deposition concentration is further increased from 3 to 5 wt%, the PWP of the composite membrane decreases gradually from 2.4 to 1.9 LMH/bar while both the NaCl and $MgCl_2$ rejections remain relatively constant. The decrease in PWP is possibly caused by the influence of two competing factors; namely, the thickness of the selective layer and the interconnectivity of the sulfonated styrene micro-domains. As mentioned earlier, the thickness of the selective layer increases with the deposition concentration, resulting in greater water transport resistance (Figure 3.6). In contrast, and at the same time, the interconnectivity of the sulfonated styrene micro-domains is likely to be enhanced with an increase in deposition concentration, thereby promoting water transport through the membrane. Thus, when the deposition concentration is at 3 to 5 wt%, the increase in selective layer thickness outweighs the enhanced interconnectivity of the sulfonated styrene micro-domains and results in a fall in PWP. On the other hand, these two competing factors appear to cancel each other out and have a negligible impact on overall salt rejections. Hence, constant NaCl and $MgCl_2$ rejections are observed when the deposition concentration increased from 3 to 5 wt%.

In order to better understand the formation of the selective layer, the micro-structure of the resultant composite membranes was investigated by PAS. Since there is no chemical difference in the resultant copolymer selective layer when using different deposition concentrations, the *S* parameter profiles

are capable of reflecting the free volume differences of the composite membranes. As seen in Figure 3.7, the composite membranes show a similar depth profile of the *S* parameter–with the curves initially exhibiting a sharp increase before gradually decreasing after reaching the peak. The initial sharp increase in *S* parameter is due to the back diffusion and scattering of positroniums near the membrane surface [27], while the gradual decrease after the peak indicates the transition from the selective layer to the bulk membrane substrate. This is because the Matrimid® substrate has negligible PAS signal due to the quenching effect of the polyimide groups [49]. However, the peaks of the depth profiles of the composite membranes show different positions and heights, indicating that the thickness as well as the free volume intensity of the copolymer selective layer changes with the deposition concentration. It can be noted that with increasing deposition concentration, the width of the peaks gradually increases. This indicates that the selective layer thickness increases with the deposition concentration. These results are in accordance with the FESEM observations in Figure 3.6. With regards to the heights of the peaks, they remain relatively constant as the deposition concentration increases from 0.5 to 3 wt%. This suggests that the free intensity volume is initially relatively independent of the deposition concentration. However, when the deposition concentration increases to 5 wt%, a significant increase in the height of the peak can be observed. This indicates that there is a significant increase of free volume intensity when the deposition concentration increases from 3 to 5 wt%. This is possibly due to the merging of some sulfonated styrene cores to form a water transport passageway which, in turns, creates more free volume. In summary, the 3 wt% deposition concentration may be the critical

concentration at which the structure of the selective layer changes from discrete sulfonated styrene cores to interconnected sulfonated styrene cores. Consequently, the resultant composite membrane displays significantly a higher PWP with no compromise in salt rejections.

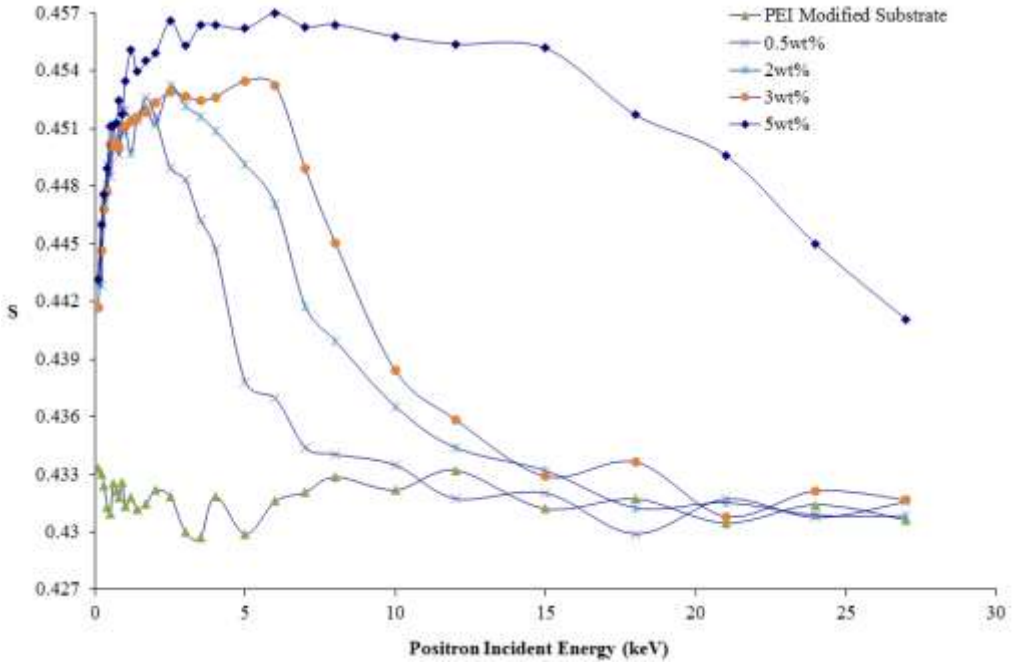

Figure 3.7 S parameters vs positron incident energy (or depth) for the composite membranes fabricated using different deposition concentrations of the copolymer.

3.4.3 Heavy metals removal

The feasibility of using these new composite NF membranes for heavy metal removal was then assessed. Table 3.2 summarizes the membrane rejections to various heavy metal ions in solutions that were prepared by directly dissolving the salts in deionized water without pH adjustment. It can be observed that the membrane has high rejections (>98%) to various heavy metal ions except for $HCrO_4^-$ (92.3%). The high membrane rejections to cations can be attributed to the small mean effective pore diameter of the composite membrane (0.50 nm), which is significantly smaller than the hydrated diameters of these cations. In addition, since the pH values of these

salt solutions are significantly below the isoelectric point of the membrane (i.e., pH 9.2), the membrane is highly positively charged under these conditions (Figure 1). As a result, the Donnan exclusion mechanism plays an additional role in effectively rejecting these cations. Consequently, with the combination of both Donnan and size exclusion, the composite membrane is able to effectively reject various cations.

Table 3.2 Rejections of heavy metal ions

Heavy metal salts (Ions)	**pH**	**Rejection (%)**	**Hydrated diameter of cations (nm)**
$Pb(NO_3)_2$, (Pb^{2+})	5.34	99.8 ± 0.2	0.802 [50]
$CdCl_2$, (Cd^{2+})	5.83	98.2 ± 0.9	0.852 [50]
$ZnCl_2$, (Zn^{2+})	5.88	99.3 ± 0.3	0.860 [50]
$NiCl_2$, (Ni^{2+})	6.58	99.8 ± 0.2	0.808 [50]
Na_2HAsO_4, ($HAsO_4^{2-}$)	8.55	99.9 ± 0.1	-
$Na_2Cr_2O_7$, ($HCrO_4^-$)	4.81	92.3 ± 0.5	-

* Model solutions containing a single heavy metal salt are used in this study. Mixed solutions are not used in this study.

In addition, the composite membrane is able to reject almost all $HAsO_4^{2-}$ ions, while showing a slightly lower rejection of about 92.3% for $HCrO_4^-$ ions. The difference in rejection to these two anions can be explained as follows: First, the $HCrO_4^-$ (MW=117.00) is likely to have a smaller hydrated diameter than $HAsO_4^{2-}$ (MW= 139.93). Therefore, $HCrO_4^-$ is able to easily permeate through the membrane, resulting in a lower rejection. Second, the higher rejection to $HAsO_4^{2-}$ may also be attributed to the differences in feed pH. The pH of the feed solution is expected to play a significant role in

determining the rejection of the NF membrane since it influences the membrane surface charge and charge density. As the feed pH of the $HAsO_4^{2-}$ solution is around the isoelectric point of the developed composite membrane, the membrane is only weakly positively charged under this condition with reduced electrostatic attraction for the $HAsO_4^{2-}$ compared to the $HCrO_4^-$ which has a feed pH much lower than the isoelectric point.

The effects of feed pH on membrane rejection and speciation of chromate ions are further studied. As illustrated in Figure 3.8, the monovalent anions of $HCrO_4^-$ are the predominant species at low pH. However, the proportion of monovalent $HCrO_4^-$ gradually decreases as the pH increases beyond 5. At around pH 6.5, the monovalent $HCrO_4^-$ and divalent CrO_4^{2-} ions co-exist in equal proportions within the solution. When the pH is greater than 6.5, the divalent CrO_4^{2-} becomes the predominant species within the solution. It is interesting to note that the rejection of chromate ions increases significantly from 78.0% to 92.3% when the pH of the solution increases from 3.06 to 4.81. Since the proportion of the monovalent anions of $HCrO_4^-$ remains constant within the entire pH range, the increase in rejection can be attributed to the significant decrease in surface charge density of the membrane (Figure 3.3). In other words, the membrane is less positively charged and electrostatic attraction between the membrane and the chromate ions are reduced. As the pH increases from 4.81 to 10.34, the rejection of chromate ions also increases gradually from 92.3% to 98.3% although the CrO_4^{2-} has a smaller hydrated diameter compared to $HCrO_4^-$. Similarly, this is likely because the composite membrane becomes less positively charged as the pH increases and eventually becomes negatively charged beyond the isoelectric point. Thus, it can be

concluded that the solution pH has a significant effect on chromate rejection because pH determines the surface charge characteristics of the membrane. With the combination of both Donnan and size exclusion at pH 10.34, the composite membrane can also effectively reject the chromate ions.

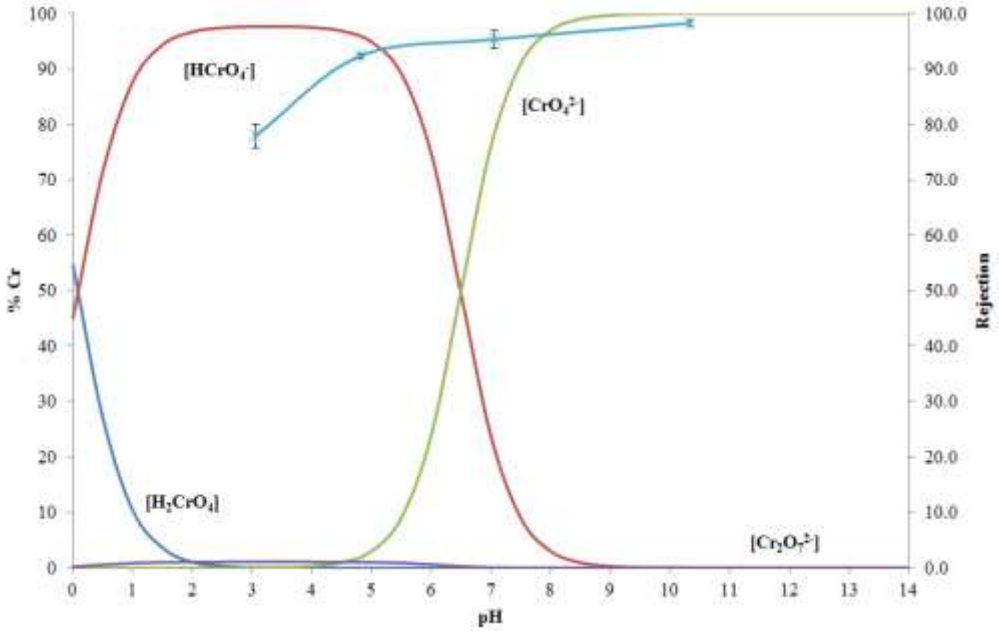

Figure 3.8 Speciation of chromate ions and rejection by the composite membrane as a function of feed solution pH. (The composite membrane was obtained using a 3wt% deposition concentration and 1 min deposition time. Feed concentration: 1000 ppm.)

Table 3.3 summarizes the separation performance of different commercial and various lab-made NF membranes reported in recent years. The commercially available membranes have a comparable PWP but lower rejections to the various heavy metals. In contrast, the previously lab-made membranes generally possess higher heavy metal rejections by sacrificing the PWP which, in turn, reflects the growing trend for having little or no contaminants in the discharge. Compared with the previously lab-made membranes, the newly developed composite NF membrane in this study shows promising rejections (>98%) against various heavy metal ions with a reasonable PWP of 2.4 LMH/bar. It is believed that the newly developed

composite membrane may be highly competitive for the removal of heavy metal ions.

Table 3.3 Comparison of NF membranes for heavy metal removal

Type of membrane	PWP (LMH/bar)	Ions	Testing Condition	Rejection	Reference
Polybenzimidazole/polyethersulfone dual layer Hollow fiber membrane	0.826	Pb^{2+},($Pb(NO_3)_2$) Cd^{2+},($CdCl_2$) Cr(VI), ($Na_2Cr_2O_7$)	Feed: 200 ppm (pH= 2.20) Feed: 200 ppm (pH = 5.45) Feed: 100 ppm (pH= 12) Pressure: 1 bar	93 95 98.9	[1]
PEI cross-linked P84 Hollow fiber membrane	0.98	Pb^{2+},($Pb(NO_3)_2$)	Feed: 1000 ppm Pressure: 13 bar	91.05	[16]
Polybenzimidazole hollow fibers	1.86	Cr(VI), ($K_2Cr_2O_7$)	Feed: 520 ppm Pressure: 20 bar pH= 12	95.7	[51]
NFI TF Composite polyamide Spiral wound	6.26 (35°C)	Cr(VI), ($K_2Cr_2O_7$)	Feed: 1000 ppm Pressure: 5 bar pH= 2 - 11	94-99*	[52]
NFII Composite polyamide Spiral wound	3.2 (35°C)	Cr(VI), ($K_2Cr_2O_7$)	Feed: 1000 ppm Pressure: 8 bar pH= 2 - 11	52-88*	
PCI membrane system AFC 80 Tubular polyamide membrane	1.2-1.3*	Pb^{2+},($Pb(NO_3)_2$)	Feed: 250 ppm Pressure: 10 bar pH= 5.8	≈98*	[53]
Dow membrane NF90 Flat sheet	7.14	Pb^{2+},($Pb(NO_3)_2$)	Feed: 20 ppm Pressure: 4.136 bar pH= 5-6	91-94	[54]
PCI membrane system AFC 30 Tubular polyamide membrane	5.9	Pb^{2+},($Pb(NO_3)_2$)	Feed: 100 ppm Pressure: 5 - 35 bar pH= 5.0	≈ 70*	[55]
Dow membrane NF270 Flat sheet	13.2	Pb^{2+},($Pb(NO_3)_2$) Cd^{2+},($Cd(NO_3)_2$)	Feed: 1000 ppm Feed: 1000 ppm Pressure: 4 bar pH= 5	≈ 60* ≈ 68*	[14]
Matrimid/PEI/Nexar Flat sheet membrane	2.4 ± 0.3	Pb^{2+},($Pb(NO_3)_2$) Cd^{2+},($CdCl_2$) As(V),(NaH_2AsO_4) Zn^{2+}, ($ZnCl_2$) Ni^{2+}, ($NiCl_2$) Cr(VI), ($Na_2Cr_2O_7$)	Feed: 1000 ppm (pH= 5.34) Feed: 1000 ppm (pH= 5.83) Feed: 1000 ppm (pH= 8.55) Feed: 1000 ppm (pH= 5.88) Feed: 1000 ppm (pH= 6.58) Feed: 1000 ppm (pH= 4.81) Pressure: 10 bar	99.8 ± 0.2 98.2 ± 0.9 99.9 ± 0.1 99.3 ± 0.3 99.8 ± 0.2 92.3 ± 0.5	This study

*Estimated from published figures

3.5 Conclusion

In this Chapter, we have successful fabricated a novel nanofiltration membrane consisting of a sulfonated pentablock copolymer rejection layer for

heavy metal removal. The NF performance, surface morphologies and transport properties of the resultant membrane have been characterized and the following conclusions can be drawn:

1. The incorporation of PEI as a gutter layer between the substrate and the selective layer is necessary because it helps to reduce the pore size of the substrate and enhance the adhesion between the substrate and selective layer.
2. The optimum deposition concentration of the pentablock copolymer is about 3wt%. The permeability of the membrane first decreases as the deposition concentration increases from 0.5 to 2wt% and then, it increases as the deposition concentration increases from 2 to 3wt%. This may be attributed to the pentablock copolymer's unique ability to form a continuous water transport passageway.
3. The resultant positively charged NF membrane can effectively remove heavy metal cations such as Pb^{2}+, Cd^{2+}, Zn^{2+} and Ni^{2+} with a rejection greater than 98.0% while having reasonably high rejections towards anions such as $HAsO_4^{2-}$ (99.9%) and $HCrO_4^{-}$ (92.3%).

4 Chapter 4 Molecular design of nanofiltration membranes for the recovery of phosphorus from sewage sludge

This chapter has been published as a journal paper

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4.1 Summary

With the rapid depletion of mineral phosphorus, the recovery of phosphorus from sewage sludge becomes increasingly important in the near future. However, the presence of various contaminants such as heavy metals in sewage sludge complicates the issue. One must separate phosphorus from the heavy metals in order to produce fertilizers of high quality. Among various available methods, nanofiltration (NF) has been demonstrated to be a feasible and promising option when the sewage sludge undergoes acidic dissolution and the operating pH is around 2. Since the performance of commercially available thin film composite (TFC) NF membranes reported thus far has great rooms for improvement, the development of highly permeable positively charged NF membranes are recommended. To this aim, a NF membrane which is desirable for phosphorus recovery was fabricated via interfacial polymerization of polyethyleneimine (PEI) and trimesoyl chloride (TMC) on a porous polyethersulfone (PES) membrane substrate. Through an optimization of the interfacial polymerization process which involves varying the molecular weight of PEI and the concentration of TMC, the resultant membrane displays a low molecular weight cut-off (MWCO) of 170 Da with a reasonably high pure water permeability of 6.4 LMH/bar. The newly developed NF membrane can effectively reject a wide variety of heavy metal ions such as Cu, Zn, Pb and Ni (>93%) while demonstrating a low phosphorus rejection of 19.6% at 10 bar using a feed solution of pH 2. Thus, up to 90% of the feed phosphorus may be recovered using this newly developed NF membrane at a permeate recovery of 90%. This is a highly competitive value for the recovery of phosphorus.

4.2 Introduction

Phosphorus is an essential nutrient for all living organisms. It is often the limiting factor for plant growth. Hence, a sufficient supply of phosphorus is necessary to maintain or improve crop yield. Based on the current agriculture practice, almost all phosphorus is provided by fertilizers. This practice is not sustainable as almost all phosphorus used in fertilizers is extracted from limited and non-renewable supplies of phosphorus rocks. The demand on exploring new phosphate rocks will increase as the world struggles to feed a rapidly growing human population. It is estimated that the mineral phosphate resources will be depleted in less than 150 years [56-59]. This calls for an urgent search for alternative sources of phosphorus. The recovery of phosphorus from urban wastewater has been identified to be a highly promising option [20-23, 60, 61].

There are several technological developments that aim to recover phosphorus from the different streams of urban wastewater. Among them, the recovery of phosphorus from sewage sludge seems to be a relatively suitable process. This is because in most wastewater treatment plants, it is often necessary to transfer all the nutrients from the wastewater to the sewage sludge to prevent possible eutrophication of water bodies. Hence, the sewage sludge acts as a significant sink for phosphorus, and it can contain up to 90% of the treatment plant's influent phosphorus [20, 22]. However, the direct usage of sewage sludge as fertilizers is usually not possible due to the presence of other toxic contaminants such as heavy metals [20-23, 60, 61]. This is because in many areas, the sewage treatment plants receive both industrial and municipal wastewater [56].

Copper (Cu), zinc (Zn), lead (Pb), nickel (Ni), chromium (Cr) and cadmium (Cd) are some heavy metals which are commonly found in sewage sludge [22]. Owing to their presence, the phosphorus recovery from sewage sludge would firstly involve the use of either acidic or alkaline dissolution of the sewage sludge to produce a phosphorus rich leachate. In the case of acidic dissolution where the operating pH is around 2 [20, 22], a variety of separation techniques such as sequential precipitation [23], sulfidic precipitation [58], cationic ion exchange [61] and nanofiltration (NF) [20, 21, 60, 62] can then be applied to remove the heavy metals from the acidic leachate and concentrate the phosphates. Subsequently, the phosphates can be precipitated from the leachate via a variety of methods to produce fertilizers which are free of contaminants and of a high quality.

Nevertheless, each of the aforementioned separation techniques has its own advantages and disadvantages. For example, NF is considered a promising separation technique for the removal of heavy metals from the acidic leachate because it requires (1) no phase change (2) small energy consumption, and (3) low chemical input [21, 60]. Theoretically, it can also provide high separation efficiency because the NF membrane possesses a positively charged surface under the acidic operation condition (of < pH 2), which enables the rejection of multivalent heavy metal cations via the size and the Donnan exclusion (electrostatic repulsion) mechanisms [1, 15, 63, 64]. In addition, phosphorus which mainly exists as un-dissociated or mono-dissociated phosphoric acid in the acidic leachate can easily permeate through the membrane due to their small hydrated diameters.

However, in reality, the performances of commercially available thin film composite (TFC) NF membranes still have rooms for improvement [22]. They tend to have a high retention rate of phosphoric acid which is undesirable for phosphorus recovery. This is because their selective layers predominantly consist of cross-linked polyamide networks prepared by interfacial polymerization of piperazine (PIP) and trimesoyl chloride (TMC) [65]. As a result, they are usually negatively charged at neutral pH and are only slightly positively charged at low pH. In addition, these commercial NF membranes are originally designed to reject divalent metal cations mainly via the size exclusion mechanism at neutral pH and hence, they tend to have a sharp pore size distribution with a tight structure [8]. Thus, the commercial TFC NF membranes often suffer from low water permeability and high retention of phosphorus due to their dense structure. Furthermore, a relatively high operating pressure is often required to achieve the desired throughput.

Issues such as severe fouling and high ionic strength of the acidic feed further reduce the membrane performance [34, 35, 45]. In order to lessen these drawbacks, Schütte *et al*. suggested the use of NF membranes that are more positively charged and permeable for the recovery of phosphorus [20]. NF membranes which have a positively charged surface at neutral pH can afford to have a relatively larger pore size to achieve higher water permeation and lower retention of phosphorus while maintaining relatively high rejections to various metal cations. This is because they can reject various metal cations via both the size and the Donnan exclusion mechanisms. Although the development of positively charged TFC NF membranes via interfacial polymerization between TMC and other amines has been widely reported [8,

66-69], there are limited studies exploring such membranes for phosphorus recovery from sewage sludge. Most studies for phosphorus recovery have been carried out using negatively charged commercial NF membranes.

Hence, the objectives of this work are to develop NF flat sheet membranes with characteristics of high permeability and positively charged surfaces and to explore them for phosphorus recovery from sewage sludge. The selective layer of the NF membranes is developed via effectively controlled interfacial polymerization between polyethyleneimine (PEI) and TMC on a porous polyethersulfone (PES) ultrafiltration membrane substrate. The pore size distribution and surface charge of the membrane have been tuned by adjusting the size of monomers and etc. to specifically reject heavy metal cations while allowing the phosphoric acid to pass through. The newly developed NF membranes were evaluated for the recovery of phosphorus using feed solutions containing a variety of heavy metal ions and phosphoric acid. This study may provide useful insights regarding the use of nanofiltration for phosphorus recovery from sewage sludge.

4.3 Materials and methods

4.3.1 Fabrication of PES substrate

The PES flat-sheet membrane substrates were fabricated via a non-solvent induced phase inversion method as described in Section 2.2. In summary, the PES substrate was fabricated by casting a polymer dope containing 20.4wt% PES, 37.7wt% NMP, 37.7wt% PEG 400 and 4.2wt% water onto a clean glass plate with a 100μm tall casting knife. Subsequently, the entire assembly was immersed in a water bath for phase inversion. After

which, the newly fabricated membrane was soaked in DI water to remove the residual NMP and PEG 400.

4.3.2 Fabrication of composite membranes via interfacial polymerization reaction

A polyamide selective layer was formed on the top surface of the PES substrate via the interfacial polymerization reaction between PEI in the aqueous phase and TMC in the organic phase. This was achieved by first soaking the PES substrate in a 3wt% PEI solution for 5 min, followed by removing the excess solution from the substrate surface with a filter paper. The PES substrate was then placed on a rectangular frame such that only the top surface was exposed to the TMC solution. Next, the prepared TMC solution was poured onto the PES substrate and then was discarded away after 1 min of reaction. It should be noted that the TMC concentration and PEI molecular weight in this study have been varied to investigate their effects on membrane performance. After which, the resultant membrane was allowed to stabilize in air for 5 min, followed by immersion in ethanol for 1 hour to facilitate the removal of n-hexane. Finally, the membrane was immersed in DI water overnight to completely remove the ethanol.

4.4 Results and discussion

4.4.1 Optimization of NF membrane

As mentioned above, the selective layer of the NF membranes was synthesized through the interfacial polymerization of PEI and TMC on a PES substrate. Since the separation performance of NF membranes is mainly determined by the properties of the selective layer, the effects of PEI molecular weight and TMC concentration on the selective layer are firstly

investigated in order to choose the optimal selective layer for phosphorus recovery. The pore size distribution of the selective layer should be designed in such a way that heavy metal cations are retained while the phosphoric acid is allowed to pass through.

Keeping the TMC and PEI concentrations constant, Figure 4.1 summarizes the effects of different PEI molecular weights on membrane performance. While there are slight variations in PWP, its value generally increases from 4.8 to 7.3 LMH/bar as the PEI molecular weight increases from 800 to 60K. In contrast, the $MgCl_2$ and NaCl rejections decrease from 98.5 to 88.2% and from 81.9 to 61.0%, respectively. These declines are due to the fact that the selective layer formed via interfacial polymerization of PEI 60K and TMC has a comparatively loose structure than that of PEI 800 and TMC because the former has (1) a lower degree of polymerization [8, 70] and (2) a smaller packing density than the latter [70].

According to previous studies [70-72], the interfacial polymerization occurs at the organic phase side of the interface rather than at the aqueous phase. Hence, the polymerization reaction is mainly controlled by the diffusion rate of PEI from the aqueous phase into the organic phase. In other words, the larger the PEI molecular weight, the slower the diffusion rate of PEI, and the lower the degree of polymerization. Consequently, when the PEI 60K monomer was used, the resultant selective layer may possess more defects with a significantly higher PWP but lower salt rejections. As shown in Figure 4.2, the surface morphologies of the fabricated membranes are relatively different. They gradually change from a “nodular-like” structure to a “ridge and valley” structure as the PEI molecular weight increases from 800 to

60K possibly due to the effects of limited PEI diffusion from the aqueous phase to the organic phase [73].

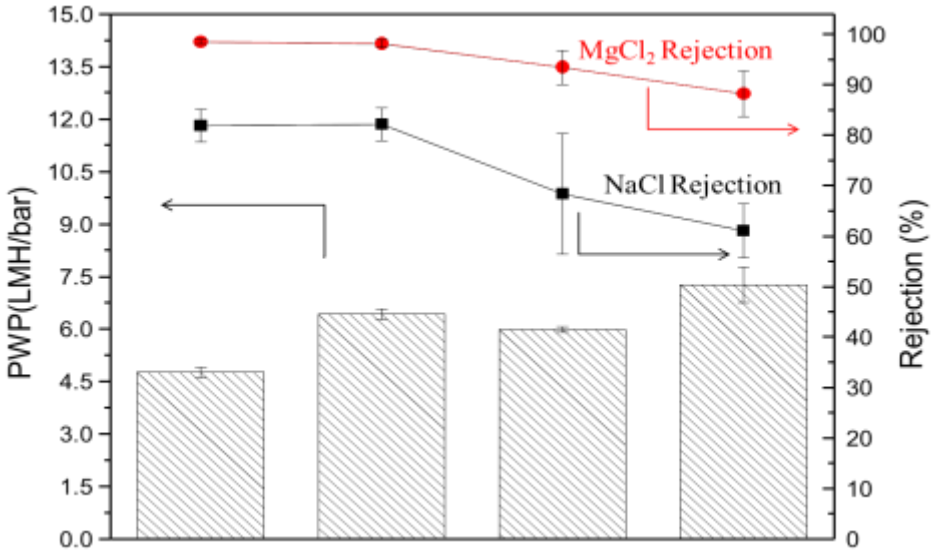

Figure 4.1 Effects of PEI molecular weight on separation performance of NF membranes. (All NF membranes were fabricated using 3 wt% PEI and 0.1 wt% TMC with a reaction time of 1 min.)

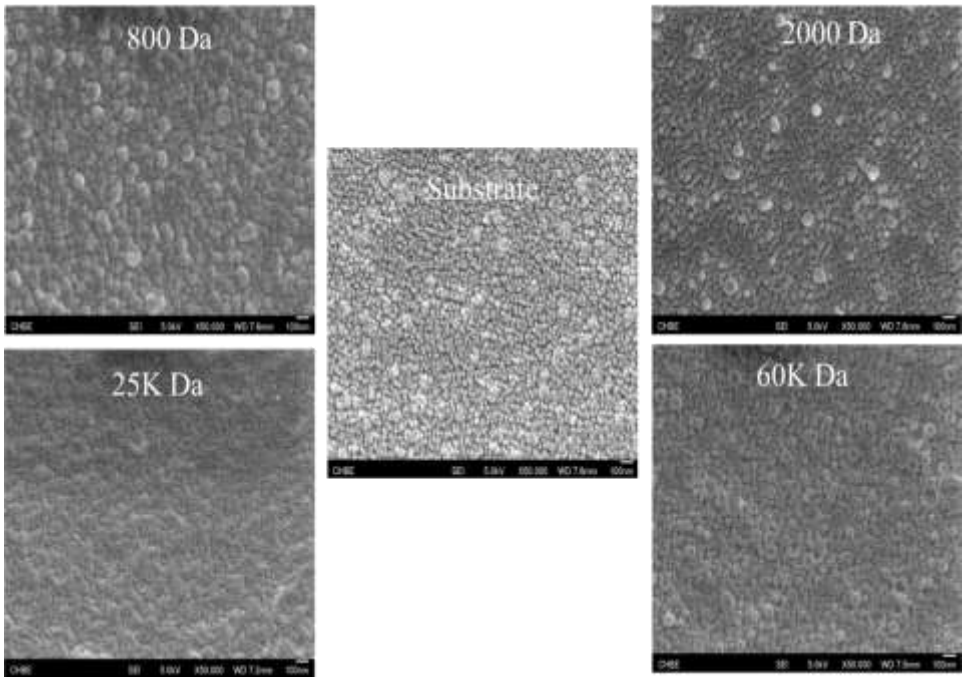

Figure 4.2 Surface morphologies of NF membranes as a function of PEI molecular weight. (All NF membranes were fabricated using 3 wt% PEI and 0.1 wt% TMC with a reaction time of 1 min.)

The PAS data reconfirm our hypothesis of forming a loose selective layer during the interfacial polymerization of TMC and PEI with a large

molecule weight. As illustrated in Figure 4.3, all NF membranes show a similar depth profile of the S parameter in which they first increase sharply before levelling off. The initial sharp increase of the S parameter is attributed to the scattering and back diffusion of positroniums near the membrane surface [26, 27, 70], while the plateau represents the selective layer as well as the bulk membrane substrate. Although there exists variations in selective layer thickness, the selective layers are generally represented by the regions between the sharp increase and 3 keV. Since there is no chemical difference between the selective layers of these NF membranes made of TMC and different PEI molecular weights, the different S parameter profiles magnify their differences in free volume [74] and micro-structure.

The S values at 3 keV shown in the small table of Figure 4.3 indicate that the free volume intensity basically increases with an increase in PEI molecular weight. The increase in free volume intensity with increasing PEI molecular weight is resulted from the fact that a high molecular weight of PEI may prevent polymer chains from packing closely together. As a consequence, the resultant selective layer has a number of free volume that facilitates a higher PWP with a lower solute rejection.

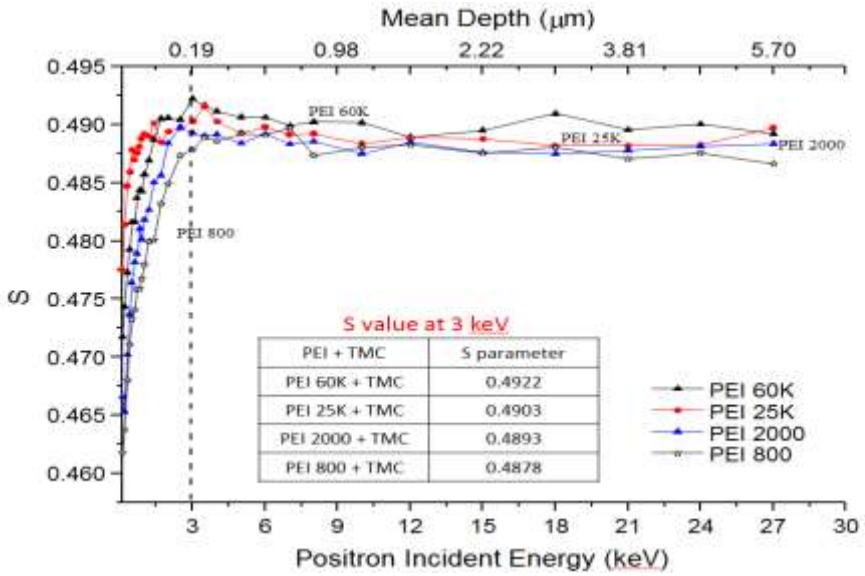

Figure 4.3 S parameters vs. positron incident energy (or depth) for the NF membranes fabricated using different PEI molecular weights.

Figure 4.4 and Table 4.1 illustrate the pore size distribution of these membranes as a function of PEI molecular weight. Consistent with PAS observation, a selective layer with a very narrow pore size distribution is formed when a PEI of small molecular weight (either 800 or 2000 Da) is used as the monomer. As a result, both the mean pore size and the MWCO are small (i.e., d_p =0.50~0.52 nm and MWCO=150 ~170 Da). In contrast, when a PEI of large molecular weight (either 25K or 60K Da) is used, the pore size distribution becomes broaden with a large mean pore size and MWCO (i.e., d_p =0.56~0.58 nm and MWCO=270~290 Da). The presence of larger pore sizes (from Figure 4.4) or holes (from Figure 4.3) indicates a lower rate of polymerization or a lower packing density when a PEI of higher molecular weight is employed as the monomer during the thin-film interfacial polymerization. Since the NF membrane synthesized from PEI 2000 appears to be most suitable in terms of water flux and pore size distribution for the recovery of phosphorus, subsequent investigations are carried out on membranes synthesized using PEI 2000.

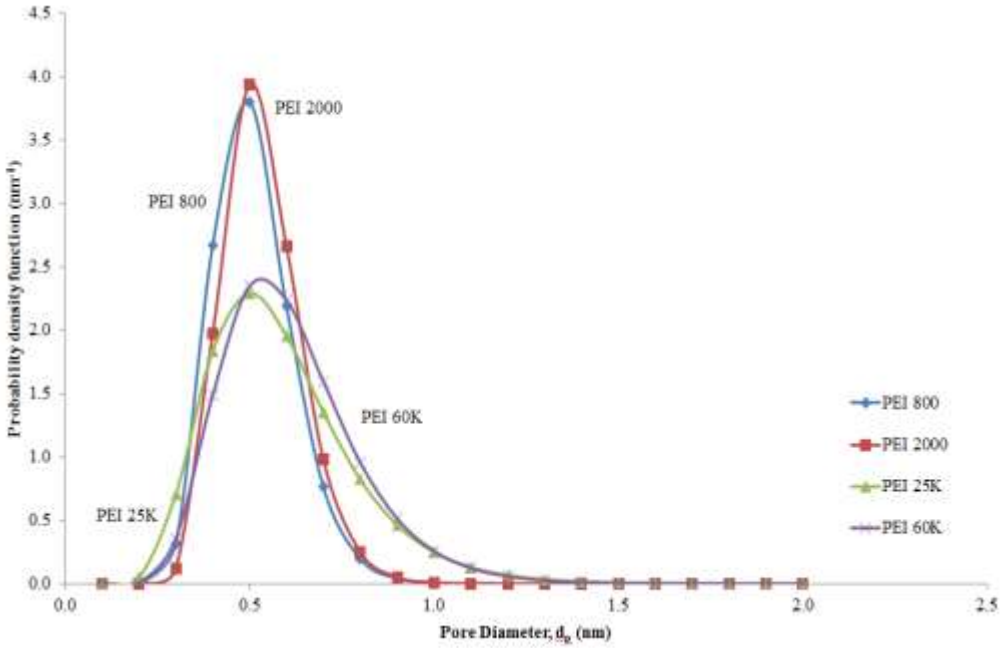

Figure 4.4 Probability density function curves of NF membranes synthesized from 3 wt% PEI with different molecular weights and 0.1 wt% of TMC with a reaction time of 1 min.

Table 4.1 Pure water permeability (PWP), mean effective pore diameter (d_p), geometric standard deviation (σ_p) and molecular cut off weight (MWCO) of the membranes.

Molecular weight of PEI	PWP (LMH/bar)*	d_p (nm)	σ_p	MWCO (Da)	MWCO equivalent diameter (nm)
Substrate (NA)	664.9 ± 47.0	16.1	1.31	148K	≈22.7
800	4.8 ± 0.2	0.50	1.23	150	≈0.65
2000	6.4 ± 0.2	0.52	1.22	170	≈0.68
25K	6.0 ± 0.1	0.56	1.39	270	≈0.85
60K	7.3 ± 0.5	0.58	1.34	290	≈0.90

* All NF membranes were synthesized from using 3 wt% PEI and 0.1 wt% TMC with a reaction time of 1min. Experimental results for all membranes except for the substrate were obtained at an trans-membrane pressure of 10 bar. An operating pressure of 1 bar was used for the substrate. The MWCO equivalent diameter refers to the diameter of solute above which the membrane can have a rejection of 90% or greater

Figure 4.5 shows the effects of TMC concentration on membrane performance. As the TMC concentration increases from 0.013 to 0.2 wt%, the PWP value decreases continuously from 7.7 to 5.7 LMH/bar. On the other hand, both the NaCl and MgCl rejections initially increase but reach plateaus at about 84% and 98% respectively when the TMC concentration is about

0.05wt% or higher because a relatively dense selective layer is formed [8], which results in a lower PWP and better salt rejections. Based on a comparison of these membranes' performance, the NF membrane synthesized from 3 wt% PEI 2000 and 0.1 wt% TMC is more suitable for subsequent studies for phosphorus recovery because it has a reasonably high PWP of 6.4 LMH/bar with a mean effective pore diameter of 0.52nm and a MWCO of 170 Da (≈0.68nm). The membrane is one that can easily reject most heavy metal cations which have a hydrated diameter of around 0.8nm (given below Table 4.2) while providing a reasonable flux.

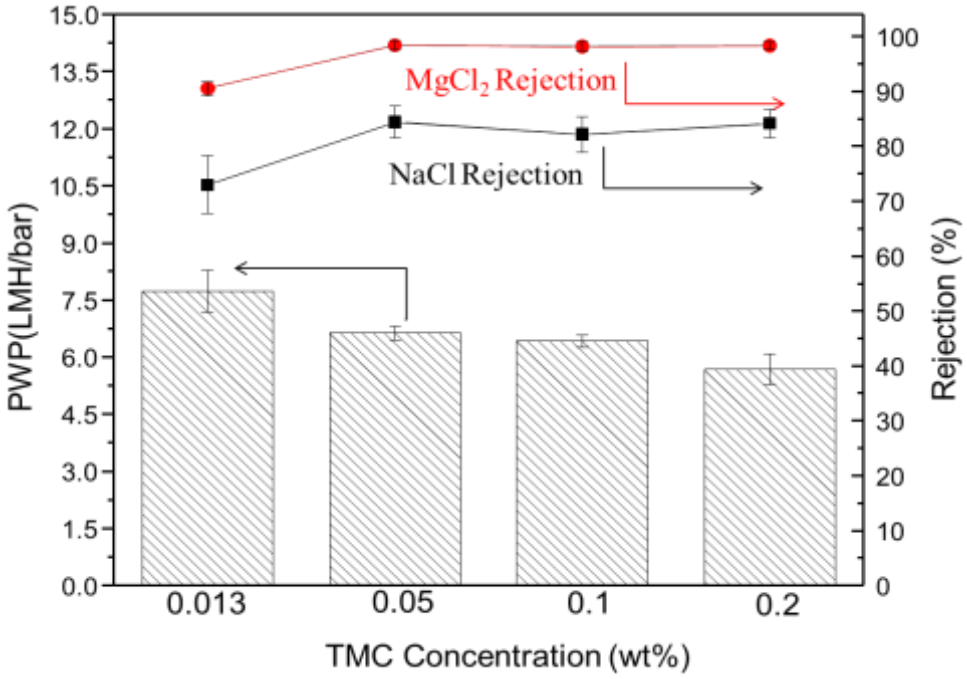

Figure 4.5 Effects of TMC concentration on NF performance. (All NF membranes were prepared using 3 wt% PEI 2000 and TMC with a reaction time of 1 min.)

4.4.2 Performance of the NF membrane in the recovery of phosphorus

As discussed in the Introduction, the applicability of the NF process for phosphorus recovery mainly depends on the principle that the NF membrane allows the preferential permeation of un-dissociated or mono-dissociated

phosphoric acid through it at low pH. Thus, in order to gain a better understanding of the transport mechanism of phosphoric acid across the nanofiltration, the effects of feed pH on the rejection and speciation of phosphoric acid have to be studied. This, in turns, will provide new insights for the design of nanofiltration membranes for better recovery of phosphorus. Figure 4.6 summarizes the results. It can be observed that the un-dissociated H_3PO_4 is prevalent at low pH. However, the proportion of the un-dissociated H_3PO_4 decreases as the pH increases. It coexists with monovalent $H_2PO_4^-$ ions in an equal proportion within the solution at about pH 2.1. The monovalent $H_2PO_4^-$ becomes the major species between pH 2.1 and 7.2, while the divalent HPO_4^{2-} ions are the predominant species between pH 7.2 and 12.7. Above pH 12.7, the phosphoric acid exists mainly as trivalent PO_4^{3-} ions. As illustrated by the dotted line, the membrane has rejection to phosphoric acid that decreases from 99.1% to 90.8% when the pH value decreases from 10.5 to 7.0, and then remains relatively stable at about 90% between pH 7.0 and 3.3. However when pH further drops from 3.3 to 2.0, the rejection to phosphoric acid decreases significantly from 89.1% to 19.6%. The observed membrane rejection to phosphoric acid as a function of pH may be explainable as follows.

Firstly, the high rejection to phosphoric acid at pH 10.5 is due to the fact that the NF membrane has a comparable MWCO equivalent diameter (i.e., 0.68nm in Table 4.1) with the hydrated diameters of HPO_4^{2-} (0.65nm) and PO_4^{3-} (0.68nm) anions [75]. Since the membrane is negatively charged at pH 10.5, as illustrated in Figure 4.7, the Donnan exclusion mechanism also plays an additional role in rejecting these anions. Thus, with a combination of both

size and Donnan exclusion, the membrane can effectively rejects almost all the phosphorus ions in this pH regime, which is not desirable for phosphorus recovery.

Secondly, only a slight drop in rejection is observed when the pH value is reduced from 10.5 to 7.0 even though the membrane has a lower surface charge density and the feed contains smaller $H_2PO_4^-$ (0.60nm) anions [75]. This implies that the dominant separation mechanism to phosphorus ions in this pH regime is the size exclusion mechanism and the Donnan exclusion mechanism plays a minor role. The size exclusion mechanism remains dominant when pH further drops from 7.0 to 3.3 because the rejection to phosphoric acid remains relatively constant at about 90% despite the membrane becoming positively charged and the attraction between the membrane surface and negatively charged phosphate ions increasing. Hence, the decline in membrane rejection from 89.1 % to 19.6% when pH drops from 3.3 to 2.0 is probably due to the much smaller hydrated diameter of the un-dissociated H_3PO_4 compared to the $H_2PO_4^-$ anions. Clearly, the pH value of the feed solution plays a critical role in determining the membrane rejection because it defines the state of phosphoric acid existing in the feed solution. In order to achieve better phosphorus recovery, the feed solution should have a pH value of preferably lower than 2. However, since the pH of sewage sludge after acidic dissolution and the long term stability pH of membranes formed by interfacial polymerization are often around 2, the subsequent investigations carried out at pH 2.

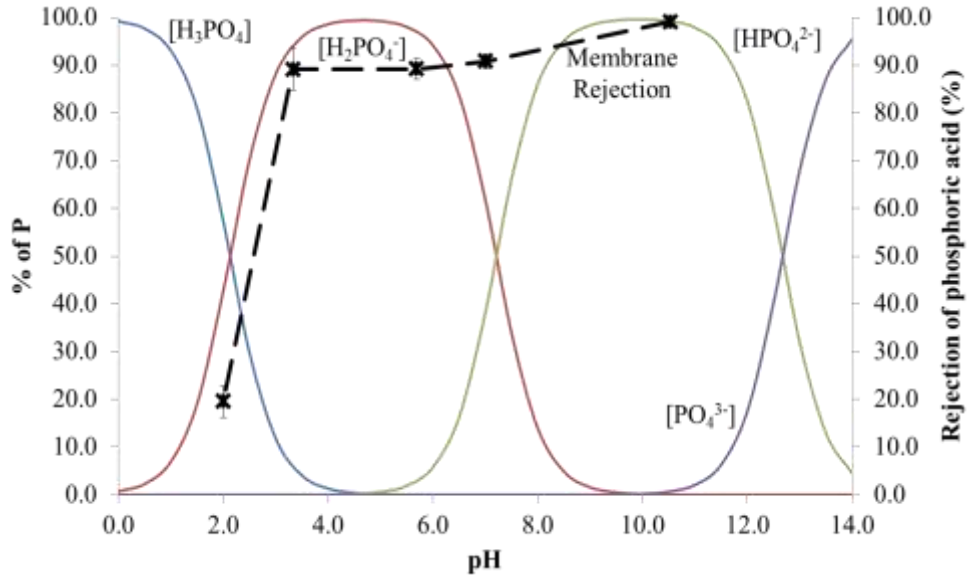

Figure 4.6 Speciation of phosphoric acid and rejection by the NF membrane as a function of feed pH. The NF membrane was prepared using 3 wt% PEI 2000 and 0.1 wt% TMC with a reaction time of 1 min. The feed concentration was 1000ppm.

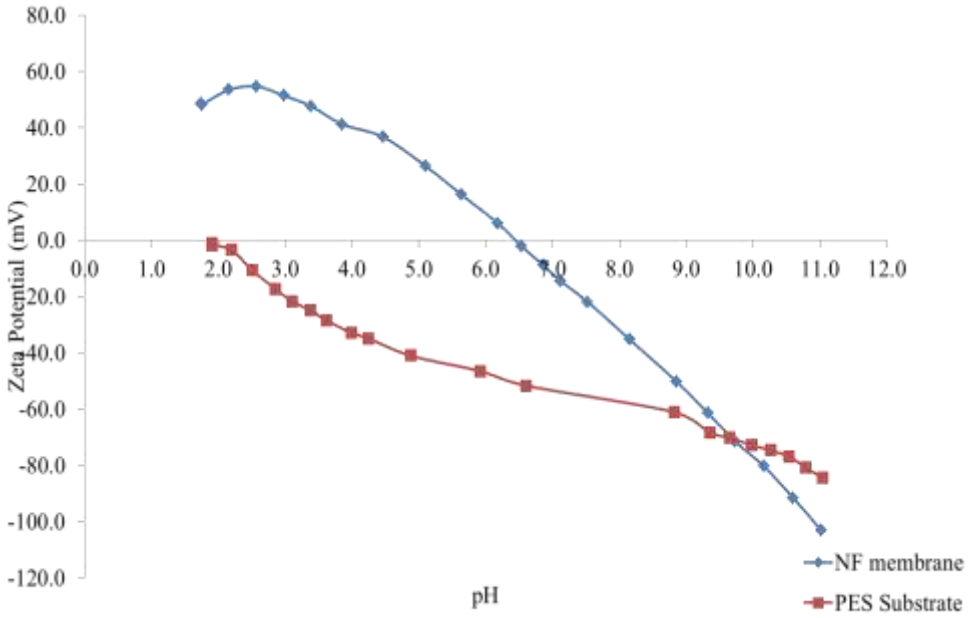

Figure 4.7 Plots of ζ potential vs. pH of the membranes. Experiments were conducted using 0.01M NaCl. The NF membrane was obtained using 3wt% PEI 2000 and 0.1wt% TMC with a reaction time of 1 min.

Figure 4.8 shows the effects of trans-membrane pressure on membrane performance. The permeate flux increases linearly with the trans-membrane pressure, while the membrane rejection to phosphoric acid remains relatively

constant at about 19%. Interestingly, the observed membrane rejection to phosphoric acid is different from previous findings where the rejection increases with the trans-membrane pressure due to hydraulic compression and dilution effect [20, 62]. This is because after the interfacial polymerization reaction, the unreacted amine groups would be protonated and have a slight positive charge when the pH value is about 2. As a result, the PEI chains within the selective layer would repel one another and create a cushion effect to mitigate the hydraulic compression. In other words, the pore size distribution of the selective layer may only change slightly under pressures due to the charge repulsion. Since the NF membrane has a pore size comparatively larger than the phosphoric acid, the combination of chain repulsion and relatively large pore in the selective layer would keep the rejection to phosphoric acid low and be independent of the trans-membrane pressure. In fact, this behavior is desirable for the industrial recovery of phosphorus since a higher operating pressure can be adopted to increase the throughput without compromising on the amount of phosphorus recovered. In summary, with an operating pressure of 10 bars and a feed solution pH of 2, the newly developed membrane can achieve a relatively low phosphoric acid rejection of about 19%.

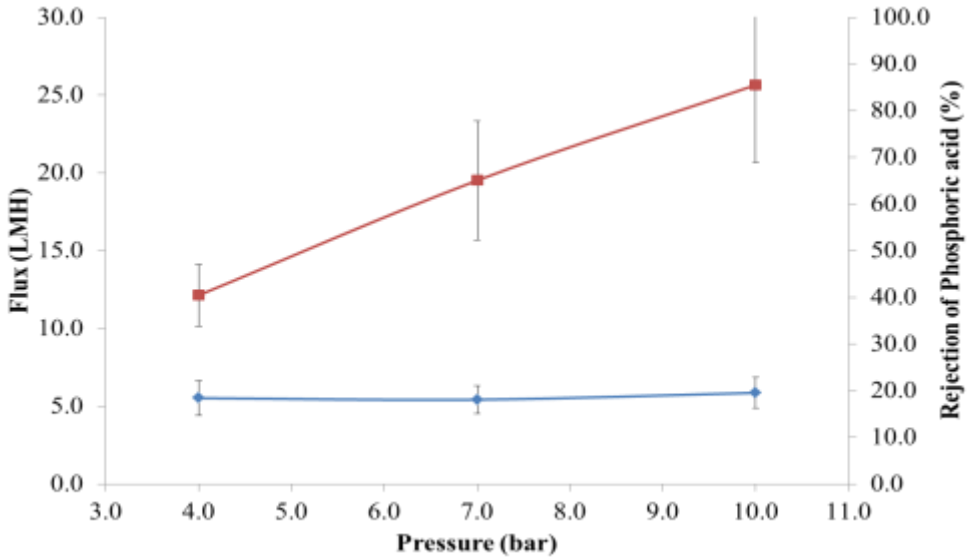

Figure 4.8 Performance of the NF membrane as a function of trans-membrane pressure. The NF membrane was obtained using 3wt% PEI 2000 and 0.1wt% TMC with a reaction time of 1 min. The feed pH was kept at 2.

4.4.3 Heavy metals removal

Given that the permeate of the NF process may be further processed as fertilizers, it is important to prevent any harmful compounds present in sewage sludge from permeating through the membrane and entering the food chain. Thus, it is necessary to assess the ability of this NF membrane for heavy metal removal. As shown in Table 4.2, it has reasonably high rejections (>93%) to various heavy metal cations commonly found in sewage sludge except Cd ions (69.6%). In principle, the membrane can effectively reject all cations via both the size and Donnan exclusion mechanisms because its MWCO equivalent diameter (0.68nm) is significantly smaller than the hydrated diameters of all the cations [50]. Also, the membrane is positively charged under these operating conditions, and there is electrostatic repulsion between the cations and the membrane. However, the rejection of Cd ions is relatively low at about 69.6% possibly due to the fact that Cd may undergo speciation and exist as Cd^{2+}, $CdCl^{+}$, $CdCl_3^{-}$ or $CdCl_4^{2-}$ at low pH [1, 76]. The presence of $CdCl_3^{-}$ or $CdCl_4^{2-}$ within the solution may lower the rejection as the Donnan exclusion

between these anions and the positively charged membrane is weak. Thus, they can permeate through the membrane more easily than cations [74]. However in reality, the amount of Cd found in sewage sludge is typically lower than the concentration used in this study. Nevertheless, additional treatment methods may be necessary when dealing with sewage sludge containing a high amount of Cd anions.

Table 4.2 The rejections of heavy metal ions by the lab-made NF membrane at 10 bar.

Heavy metal salts (Ions)	pH of salt solutions	Rejection of heavy metal ions(%)	Hydrated diameter of ions (nm)
$Pb(NO_3)_2$, (Pb^{2+})	2.0	93.4 ± 1.8	0.802 [50]
$NiCl_2$, (Ni^{2+})	2.0	99.2 ± 0.3	0.808 [50]
$CuSO_4$, (Cu^{2+})	2.0	96.7 ± 0.6	0.838 [50]
$CdCl_2$, (Cd^{2+})	2.0	69.6 ± 5.8	0.852 [50]
$ZnCl_2$, (Zn^{2+})	2.0	94.2 ± 2.3	0.860 [50]

* Model solutions containing a single heavy metal salt are used in this study. Mixed solutions are not used in this study.

After which, the separation performance of the lab-made NF membrane is compared with those of other commercial NF membranes. As illustrated in Table 4.3, the commercially available membranes except NF 270 tend to have relatively low PWP values of 1.1~4.1 LMH/bar but comparable rejections to lead. NF 270 has a higher PWP possibly because it has a larger MWCO compared to the rest of the membranes. In contrast, most commercial membranes have a phosphorus rejection of about 50 to 60% except As, which has a slightly lower rejection of about 38%. However, the rejection of these

commercial membranes to phosphorous should be further reduced in order to have a better phosphorous recovery. According to Blöcher *et al*., 68% of the feed phosphorus may be recovered if the permeate recovery (which is a ratio of the permeated volume to the feed volume) is kept at 90% and the membrane has a phosphorus rejection of 50% [60]. Assuming the same permeate recovery of 90%, the phosphorus recovery can be further increased to 82% and 90% if the membrane rejection of phosphoric can be reduced to 40% and 20%, respectively [60]. As a result, the newly developed NF membrane may be highly competitive for phosphorus recovery from sewage sludge because it has a very low phosphoric rejection of only 20%.

Table 4.3 Comparison of nanofiltration membranes.

Type of membrane	PWP ($L/m^2.hr.bar$)	MWCO	Testing Condition	Rejection of Pb (%)	Rejection of Phosphorus (%)	Reference
NF270	8.6	200-400	10 bar, pH 1.5	≈ 99*	≈58*	[20]
DL	4.1	150-300	10 bar, pH 1.5	≈ 99*	≈62*	[20]
As	1.1	180	10 bar, pH 0.5	≈ 88*	≈38*	[20]
Duracid	1.1	NIL	10 bar, pH 0.5	≈93*	≈50*	[20]
Lab-made Membrane	6.4 ± 0.2	170	10 bar, pH 2	93.4 ± 1.8	19.6 ± 3.3	This study

*Estimated from published figures. The feed consisted of digested sewage sludge which had been subjected to acidic dissolution with sulphuric acid and ultrafiltration pretreatment. The feed comprised mainly of sulphur (4420ppm), iron (1280ppm), phosphorus (820ppm) and a variety of heavy metals around 1.4ppm.

4.5 Conclusion

In this study, we have successfully fabricated a positively charged NF that is capable of recovering phosphorus from sewage sludge and revealed the basic science behind it. The following conclusions can be drawn from this study:

1. During the interfacial polymerization of PEI and TMC, the pore size distribution of the selective layer can be optimised by varying the molecular weight of PEI. The smaller the PEI, the smaller the mean pore size and MWCO of the resultant selective layer.
2. A feed solution pH of lower than 2.1 is necessary for the required for a low retention of phosphorus. This is because at a pH lower than 2, the phosphoric acids are present in the un-dissociated forms with relatively smaller hydrated diameters. Then they can easily pass through the membrane.
3. The newly developed NF membrane can effectively reject heavy metal ions such as Cu, Zn, Pb and Ni (>93%) while demonstrating a low phosphorus rejection of 19.6% at 10 bar using a feed solution of pH 2.
4. Assuming a permeate recovery of 90%, up to 90% of the feed phosphorus may be recovered. This is a highly competitive value for the recovery of phosphorus.

5 Chapter 5 Conclusion

As discussed in the above sections, the two main objectives of this dissertation are (1) the development of a composite NF membrane which comprises of a pentablock copolymer selective layer for the removal of heavy metal ions (Chapter 3) and (2) the conceptual demonstration of the recovery of phosphates and removal of heavy metal ions from sewage sludge to address the rapid depletion of mineral phosphorus (Chapter 4).

With regards to first objective of developing a composite NF membrane which comprises of a pentablock copolymer selective layer for the removal of heavy metal ions, the follow conclusions can be drawn:

1) The molecularly designed pentablock copolymer has the potential to be an alternative selective layer material for nanofiltration membranes since the newly developed nanofiltration membrane has a relatively low molecular weight cut-off of 255 Da and a reasonably high pure water permeability of 2.4 LMH/bar. High rejections of the various heavy metal ions have also been reported.
2) The pentablock copolymer's unique ability to form a continuous water transport passageway with a defined pore size represents a possible way to overcome the trade-off between selectively and permeability. The continuous water transport passageway lowers the transport resistance of the membrane towards water while maintaining a high selectivity.

However, there are also a few points that are worthy of further investigations:

1) Based on the current method of fabrication, the thickness of the pentablock copolymer selective layer should not and cannot be further reduced. As a result of that, the selective layer has a thickness of 1.05µm which is significantly greater than the 100nm of the current state-of-the-art polyamide selective layer. Despite the presence of a continuous water transport passageway which lowers water transport resistance, the permeability of the newly developed NF membranes is still significantly lower than that of the commercially available polyamide NF membranes. Hence, it is of interest in future works to develop new fabrication methods which helps to lower the thickness of the selective layer while maintaining its selectivity.

With regards to second objective of the conceptual demonstration of the recovery of phosphates and removal of heavy metal ions from sewage sludge to address the rapid depletion of mineral phosphorus, the follow conclusions can be drawn:

1) The recovery of phosphates and removal of heavy metal ions from sewage sludge using nanofiltration is highly possible. Using single component model solutions, NF membrane can effectively reject heavy metal ions such as Cu, Zn, Pb and Ni (>93%) while demonstrating a low phosphorus rejection of 19.6% at 10 bar using a feed solution of pH 2.
2) A feed solution pH of lower than 2.1 is necessary for the required for a low retention of phosphorus. This is because at a pH lower than 2, the phosphoric acids can easily pass through the membrane. Assuming a

permeate recovery of 90%, up to 90% of the feed phosphorus may be recovered. This is a highly competitive value.

However, there are also a few points that are worthy of further investigations:

1) Given that only model solutions have been used in this study, it is interesting to explore the performance of the NF membrane using real sewage sludge which has lower concentrations of heavy metal ions and phosphates.
2) The economical assessment of recovering phosphates from sewage sludge should be conducted as well.

6 References

[1] W.-P. Zhu, S.-P. Sun, J. Gao, F.-J. Fu, T.-S. Chung, Dual-layer polybenzimidazole/polyethersulfone (PBI/PES) nanofiltration (NF) hollow fiber membranes for heavy metals removal from wastewater, Journal of Membrane Science, 456 (2014) 117-127.

[2] S. Zhang, F. Fu, T.-S. Chung, Substrate modifications and alcohol treatment on thin film composite membranes for osmotic power, Chemical Engineering Science, 87 (2013) 40-50.

[3] S. Zhang, L. Luo, Z.W. Thong, T.S. Chung, Materials for Water Remediation (Membranes), in: 50 Years of Materials Science in Singapore, WORLD SCIENTIFIC, 2016, pp. 37-74.

[4] Y.K. Ong, F.Y. Li, S.-P. Sun, B.-W. Zhao, C.-Z. Liang, T.-S. Chung, Nanofiltration hollow fiber membranes for textile wastewater treatment: Lab-scale and pilot-scale studies, Chemical Engineering Science, 114 (2014) 51-57.

[5] L. Shao, X.Q. Cheng, Y. Liu, S. Quan, J. Ma, S.Z. Zhao, K.Y. Wang, Newly developed nanofiltration (NF) composite membranes by interfacial polymerization for Safranin O and Aniline blue removal, Journal of Membrane Science, 430 (2013) 96-105.

[6] S.P. Sun, T.A. Hatton, T.-S. Chung, Hyperbranched Polyethyleneimine Induced Cross-Linking of Polyamide−imide Nanofiltration Hollow Fiber Membranes for Effective Removal of Ciprofloxacin, Environmental Science & Technology, 45 (2011) 4003-4009.

[7] K.Y. Wang, T.-S. Chung, Polybenzimidazole nanofiltration hollow fiber for cephalexin separation, AIChE Journal, 52 (2006) 1363-1377.

[8] W. Fang, L. Shi, R. Wang, Interfacially polymerized composite nanofiltration hollow fiber membranes for low-pressure water softening, Journal of Membrane Science, 430 (2013) 129-139.

[9] Y. Cui, Q. Ge, X.-Y. Liu, T.-S. Chung, Novel forward osmosis process to effectively remove heavy metal ions, Journal of Membrane Science, 467 (2014) 188-194.

[10] Y. Cui, H. Wang, H. Wang, T.-S. Chung, Micro-morphology and formation of layer-by-layer membranes and their performance in osmotically driven processes, Chemical Engineering Science, 101 (2013) 13-26.

[11] Y. Cui, X.-Y. Liu, T.-S. Chung, Enhanced osmotic energy generation from salinity gradients by modifying thin film composite membranes, Chemical Engineering Journal, 242 (2014) 195-203.

[12] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, Journal of Environmental Management, 92 (2011) 407-418.

[13] J. Lv, K.Y. Wang, T.-S. Chung, Investigation of amphoteric polybenzimidazole (PBI) nanofiltration hollow fiber membrane for both cation and anions removal, Journal of Membrane Science, 310 (2008) 557-566.

[14] B.A.M. Al-Rashdi, D.J. Johnson, N. Hilal, Removal of heavy metal ions by nanofiltration, Desalination, 315 (2013) 2-17.

[15] W. Peng, I.C. Escobar, Rejection Efficiency of Water Quality Parameters by Reverse Osmosis and Nanofiltration Membranes, Environmental Science & Technology, 37 (2003) 4435-4441.

[16] J. Gao, S.-P. Sun, W.-P. Zhu, T.-S. Chung, Polyethyleneimine (PEI) cross-linked P84 nanofiltration (NF) hollow fiber membranes for Pb^{2+} removal, Journal of Membrane Science, 452 (2014) 300-310.

[17] B. Al-Rashdi, C. Somerfield, N. Hilal, Heavy Metals Removal Using Adsorption and Nanofiltration Techniques, Separation & Purification Reviews, 40 (2011) 209-259.

[18] M.A. Barakat, New trends in removing heavy metals from industrial wastewater, Arabian Journal of Chemistry, 4 (2011) 361-377.

[19] S.-P. Sun, T.-S. Chung, K.-J. Lu, S.-Y. Chan, Enhancement of flux and solvent stability of Matrimid® thin-film composite membranes for organic solvent nanofiltration, AIChE Journal, 60 (2014) 3623-3633.

[20] T. Schütte, C. Niewersch, T. Wintgens, S. Yüce, Phosphorus recovery from sewage sludge by nanofiltration in diafiltration mode, Journal of Membrane Science, 480 (2015) 74-82.

[21] C. Niewersch, C.N. Koh, T. Wintgens, T. Melin, C. Schaum, P. Cornel, Potentials of using nanofiltration to recover phosphorus from sewage sludge, Water Science and Technology, 57 (2008) 707-714.

[22] S. Petzet, B. Peplinski, P. Cornel, On wet chemical phosphorus recovery from sewage sludge ash by acidic or alkaline leaching and an optimized combination of both, Water Research, 46 (2012) 3769-3780.

[23] M. Takahashi, S. Kato, H. Shima, E. Sarai, T. Ichioka, S. Hatyakawa, H. Miyajiri, Technology for recovering phosphorus from incinerated wastewater treatment sludge, Chemosphere, 44 (2001) 23-29.

[24] C. Ba, J. Langer, J. Economy, Chemical modification of P84 copolyimide membranes by polyethylenimine for nanofiltration, Journal of Membrane Science, 327 (2009) 49-58.

[25] G. Han, S. Zhang, X. Li, T.-S. Chung, High performance thin film composite pressure retarded osmosis (PRO) membranes for renewable salinity-gradient energy generation, Journal of Membrane Science, 440 (2013) 108-121.

[26] Y.C. Jean, W.-S. Hung, C.-H. Lo, H. Chen, G. Liu, L. Chakka, M.-L. Cheng, D. Nanda, K.-L. Tung, S.-H. Huang, K.-R. Lee, J.-Y. Lai, Y.-M. Sun, C.-C. Hu, C.-C. Yu, Applications of positron annihilation spectroscopy to polymeric membranes, Desalination, 234 (2008) 89-98.

[27] H. Chen, W.-S. Hung, C.-H. Lo, S.-H. Huang, M.-L. Cheng, G. Liu, K.-R. Lee, J.-Y. Lai, Y.-M. Sun, C.-C. Hu, R. Suzuki, T. Ohdaira, N. Oshima, Y.C. Jean, Free-Volume Depth Profile of Polymeric Membranes Studied by Positron Annihilation Spectroscopy: Layer Structure from Interfacial Polymerization, Macromolecules, 40 (2007) 7542-7557.

[28] B. Van der Bruggen, C. Vandecasteele, Modelling of the retention of uncharged molecules with nanofiltration, Water Research, 36 (2002) 1360-1368.

[29] P. Aimar, M. Meireles, V. Sanchez, A contribution to the translation of retention curves into pore size distributions for sieving membranes, Journal of Membrane Science, 54 (1990) 321-338.

[30] S. Singh, K.C. Khulbe, T. Matsuura, P. Ramamurthy, Membrane characterization by solute transport and atomic force microscopy, Journal of Membrane Science, 142 (1998) 111-127.

[31] K.Y. Wang, T.-S. Chung, The characterization of flat composite nanofiltration membranes and their applications in the separation of Cephalexin, Journal of Membrane Science, 247 (2005) 37-50.

[32] T.A. Kurniawan, G.Y.S. Chan, W.-H. Lo, S. Babel, Physico–chemical treatment techniques for wastewater laden with heavy metals, in: Chemical Engineering Journal, 2006, pp. 83-98.

[33] H.A. Qdais, H. Moussa, Removal of heavy metals from wastewater by membrane processes: a comparative study, Desalination, 164 (2004) 105-110.

[34] B. Van der Bruggen, L. Lejon, C. Vandecasteele, Reuse, Treatment, and Discharge of the Concentrate of Pressure-Driven Membrane Processes, Environmental Science & Technology, 37 (2003) 3733-3738.

[35] B. Van der Bruggen, M. Mänttäri, M. Nyström, Drawbacks of applying nanofiltration and how to avoid them: A review, Separation and Purification Technology, 63 (2008) 251-263.

[36] G. Han, T.-S. Chung, M. Toriida, S. Tamai, Thin-film composite forward osmosis membranes with novel hydrophilic supports for desalination, Journal of Membrane Science, 423–424 (2012) 543-555.

[37] R.J. Petersen, Composite reverse osmosis and nanofiltration membranes, Journal of Membrane Science, 83 (1993) 81-150.

[38] G.M. Geise, C.L. Willis, C.M. Doherty, A.J. Hill, T.J. Bastow, J. Ford, K.I. Winey, B.D. Freeman, D.R. Paul, Characterization of Aluminum-Neutralized Sulfonated Styrenic Pentablock Copolymer Films, Industrial & Engineering Chemistry Research, 52 (2012) 1056-1068.

[39] G.M. Geise, H.-S. Lee, D.J. Miller, B.D. Freeman, J.E. McGrath, D.R. Paul, Water purification by membranes: The role of polymer science, Journal of Polymer Science Part B: Polymer Physics, 48 (2010) 1685-1718.

[40] J.H. Choi, C.L. Willis, K.I. Winey, Effects of neutralization with Et3Al on structure and properties in sulfonated styrenic pentablock copolymers, Journal of Membrane Science, 428 (2013) 516-522.

[41] J.-H. Choi, C.L. Willis, K.I. Winey, Structure–property relationship in sulfonated pentablock copolymers, Journal of Membrane Science, 394–395 (2012) 169-174.

[42] G.M. Geise, B.D. Freeman, D.R. Paul, Characterization of a sulfonated pentablock copolymer for desalination applications, Polymer, 51 (2010) 5815-5822.

[43] S.P. Sun, K.Y. Wang, N. Peng, T.A. Hatton, T.-S. Chung, Novel polyamide-imide/cellulose acetate dual-layer hollow fiber membranes for nanofiltration, Journal of Membrane Science, 363 (2010) 232-242.

[44] L. Setiawan, R. Wang, K. Li, A.G. Fane, Fabrication of novel poly(amide–imide) forward osmosis hollow fiber membranes with a positively charged nanofiltration-like selective layer, Journal of Membrane Science, 369 (2011) 196-205.

[45] C. Ba, D.A. Ladner, J. Economy, Using polyelectrolyte coatings to improve fouling resistance of a positively charged nanofiltration membrane, Journal of Membrane Science, 347 (2010) 250-259.

[46] P.H.H. Duong, T.-S. Chung, S. Wei, L. Irish, Highly permeable double-skinned forward osmosis membranes for anti-fouling in the emulsified oil-water separation process, Environmental science & technology, 48 (2014) 4537.

[47] R. Gao, D. Wang, J.R. Heflin, T.E. Long, Imidazolium sulfonate-containing pentablock copolymer-ionic liquid membranes for electroactive actuators, Journal of Materials Chemistry, 22 (2012) 13473-13476.

[48] J.-H. Choi, A. Kota, K.I. Winey, Micellar Morphology in Sulfonated Pentablock Copolymer Solutions, Industrial & Engineering Chemistry Research, 49 (2010) 12093-12097.

[49] V.P. Shantarovich, T. Suzuki, C. He, V.W. Gustov, Inhibition of positronium formation by polar groups in polymers—relation with TSL experiments, Radiation Physics and Chemistry, 67 (2003) 15-23.

[50] E.R. Nightingale Jr., Phenomenological Theory of Ion Solvation. Effective Radii of Hydrated Ions, The Journal of Physical Chemistry, 63 (1959) 1381-1387.

[51] K.Y. Wang, T.-S. Chung, Fabrication of polybenzimidazole (PBI) nanofiltration hollow fiber membranes for removal of chromate, Journal of Membrane Science, 281 (2006) 307-315.

[52] M. Muthukrishnan, B.K. Guha, Effect of pH on rejection of hexavalent chromium by nanofiltration, Desalination, 219 (2008) 171-178.

[53] C.-V. Gherasim, P. Mikulášek, Influence of operating variables on the removal of heavy metal ions from aqueous solutions by nanofiltration, Desalination, 343 (2014) 67-74.

[54] W. Saikaew, S. Mattaraj, R. Jiraratananon, Nanofiltration performance of lead solutions: effects of solution pH and ionic strength, Water Science & Technology: Water Supply, 10 (2010) 193.

[55] S. Bouranene, P. Fievet, A. Szymczyk, M. El-Hadi Samar, A. Vidonne, Influence of operating conditions on the rejection of cobalt and lead ions in aqueous solutions by a nanofiltration polyamide membrane, Journal of Membrane Science, 325 (2008) 150-157.

[56] D. Cordell, J.-O. Drangert, S. White, The story of phosphorus: Global food security and food for thought, Global Environmental Change, 19 (2009) 292-305.

[57] V. Smil, Phosphorus in the environment: Natural Flows and Human Interferences, Annual Review of Energy and the Environment, 25 (2000) 53-88.

[58] M. Franz, Phosphate fertilizer from sewage sludge ash (SSA), Waste Management, 28 (2008) 1809-1818.

[59] J. Driver, D. Lijmbach, I. Steen, Why Recover Phosphorus for Recycling, and How?, Environmental Technology, 20 (1999) 651-662.

[60] C. Blöcher, C. Niewersch, T. Melin, Phosphorus recovery from sewage sludge with a hybrid process of low pressure wet oxidation and nanofiltration, Water Research, 46 (2012) 2009-2019.

[61] S. Donatello, D. Tong, C.R. Cheeseman, Production of technical grade phosphoric acid from incinerator sewage sludge ash (ISSA), Waste Management, 30 (2010) 1634-1642.

[62] C. Niewersch, K. Meier, T. Wintgens, T. Melin, Selectivity of polyamide nanofiltration membranes for cations and phosphoric acid, Desalination, 250 (2010) 1021-1024.

[63] S. Zhang, M.H. Peh, Z. Thong, T.-S. Chung, Thin Film Interfacial Cross-Linking Approach To Fabricate a Chitosan Rejecting Layer over Poly(ether sulfone) Support for Heavy Metal Removal, Industrial & Engineering Chemistry Research, 54 (2015) 472-479.

[64] C.E. Isabel, B. Bart Van der, Introduction, in: Modern Applications in Membrane Science and Technology, American Chemical Society, 2011, pp. 1-4.

[65] J. Schaep, C. Vandecasteele, Evaluating the charge of nanofiltration membranes, Journal of Membrane Science, 188 (2001) 129-136.

[66] S.P. Sun, T.A. Hatton, S.Y. Chan, T.-S. Chung, Novel thin-film composite nanofiltration hollow fiber membranes with double repulsion for effective removal of emerging organic matters from water, Journal of Membrane Science, 401–402 (2012) 152-162.

[67] Y.-C. Chiang, Y.-Z. Hsub, R.-C. Ruaan, C.-J. Chuang, K.-L. Tung, Nanofiltration membranes synthesized from hyperbranched polyethyleneimine, Journal of Membrane Science, 326 (2009) 19-26.

[68] S. Veríssimo, K.V. Peinemann, J. Bordado, Influence of the diamine structure on the nanofiltration performance, surface morphology and surface charge of the composite polyamide membranes, Journal of Membrane Science, 279 (2006) 266-275.

[69] L. Lianchao, W. Baoguo, T. Huimin, C. Tianlu, X. Jiping, A novel nanofiltration membrane prepared with PAMAM and TMC by in situ interfacial polymerization on PEK-C ultrafiltration membrane, Journal of Membrane Science, 269 (2006) 84-93.

[70] J. Zuo, Y. Wang, S.P. Sun, T.-S. Chung, Molecular design of thin film composite (TFC) hollow fiber membranes for isopropanol dehydration via pervaporation, Journal of Membrane Science, 405–406 (2012) 123-133.

[71] V. Freger, Kinetics of Film Formation by Interfacial Polycondensation, Langmuir, 21 (2005) 1884-1894.

[72] J.E. Cadotte, R.J. Petersen, R.E. Larson, E.E. Erickson, A new thin-film composite seawater reverse osmosis membrane, Desalination, 32 (1980) 25-31.

[73] X. Li, K.Y. Wang, B. Helmer, T.-S. Chung, Thin-Film Composite Membranes and Formation Mechanism of Thin-Film Layers on Hydrophilic

Cellulose Acetate Propionate Substrates for Forward Osmosis Processes, Industrial & Engineering Chemistry Research, 51 (2012) 10039-10050.

[74] Z. Thong, G. Han, Y. Cui, J. Gao, T.-S. Chung, S.Y. Chan, S. Wei, Novel Nanofiltration Membranes Consisting of a Sulfonated Pentablock Copolymer Rejection Layer for Heavy Metal Removal, Environmental Science & Technology, 48 (2014) 13880-13887.

[75] M.Y. Kiriukhin, K.D. Collins, Dynamic hydration numbers for biologically important ions, Biophysical Chemistry, 99 (2002) 155-168.

[76] S. Pivovarov, Modeling of ionic equilibria of trace metals (Cu^{2+}, Zn^{2+}, Cd^{2+}) in concentrated aqueous electrolyte solutions at 25 °C, Journal of Colloid and Interface Science, 291 (2005) 421-432.